Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
University of Messina, Sicily, Italy

Third International Conference
CATALYSIS FOR RENEWABLE SOURCES: FUEL, ENERGY, CHEMICALS
CRS-3

September 6-11, 2015, Catania, Sicily, Italy

ABSTRACTS

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Третья Международная конференция "КАТАЛИЗ ДЛЯ ПЕРЕРАБОТКИ ВОЗОБНОВЛЯЕМОГО СЫРЬЯ: ТОПЛИВО, ЭНЕРГИЯ, ХИМИЧЕСКИЕ ПРОДУКТЫ".
Сборник тезисов докладов

Сборник включает тезисы пленарных, ключевых лекций, устных и стендовых докладов секций:

- **I. Catalysis in dendrochemistry for valuables production**
  - Catalytic systems for hemicellulose depolymerization
  - Catalytic processing of tall oil and tar, Selective conversion of sugars
  - Catalytic transformations of CO2 to fine chemicals
- **II. Biomass derivatives in petrochemistry**
  - Catalyst application for clean syn-gas and clean hydrogen production
  - Lipids in petrochemical synthesis
- **III. Catalytic processes for biofuels production**
  - Catalytic interesterification and hydrocracking of lipids to kerosene and diesel fractions
  - Catalytic approaches for the processing of pyrolysis biomass products
- **IV. Bio-Photo-/Electro-catalytic conversion of renewables**
  - Bio-catalysis for chemicals production
  - Photo-catalytic for environmental protection
  - Electro-catalytic conversion of renewables

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PLENARY LECTURES

INTEGRATING BIO- AND SOLAR- REFINERIES: AN EFFECTIVE NEW OPTION

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Biomass as chemical feedstock, (re)use of CO_2, waste valorization and use of renewable energy are some of the elements characterizing the new scenario for sustainable (low-carbon) chemical and energy production. While new drivers are moving the scenario for biorefineries towards the concept of biofactories, an important element in this direction will be also the integration of bio- and solar-refineries, in order to exploit and valorize the CO_2 produced in biorefineries as well as to integrate renewable energy sources in biorefinery production (solar biorefineries).

The integration of the use of emitted CO_2 in biorefineries schemes, especially by using renewable energy sources in these conversion processes, is the necessary direction to reduce the environmental impact of biofuel production. In addition, various opportunities derive from this concept to increase the productivity, to diversity the production and valorize the byproducts, as well as to realize symbiosis with other industries. Furthermore, many agro-industry processes have large emitted amounts of CO_2, which offer similar possibilities to combine a reduction of GHG emissions and at the same time improve economics of the whole process.

This lecture will first introduce these aspects and the drivers and opportunities in moving to new models of sustainable biorefineries, with focus on the exploitation and valorization of nearly-pure CO_2 produced in biorefineries (by fermentation and recovery from biogas) and the opportunities to integrate renewable energy sources in the biorefinery production (solar biorefineries).

The drivers to move from biorefineries to biofactories and the possible models (olefin biofactories and intermediate/high-added value chemicals biofactories) will be analyzed, with focus on the status of catalysis research to enable the development of these biorefinery models, together with an analysis of the industrial developments in the field and some elements of assessment of the different routes. The options to integrate the utilization of CO_2 within bioeconomy will be also presented, with some indications about the cost-effectiveness of solar energy integration.

PL-2

PERSPECTIVE CATALYTIC REACTIONS FOR DIRECT FUELS AND BULK CHEMICALS PRODUCTION BASED ON BIO OXYGENATES

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Keywords: alcohols, rapeseed oil, catalysts, structure, bimetallic active components, catalytic activity and selectivity, hydrocarbon fuel, chemicals

Introduction

Ethanol, 2-methylpropanol-1, 3-methylbutanol-1, mixture of fermentation organic products, glycerol and rapeseed oil are known to give rise bio-fuel components under hydro-deoxygenation conditions. Selective conversions of bio-substrates into alkanes, olefins, aromatics and naphthenic hydrocarbons components of gasoline and diesel fractions as well as n-butanol and pentanol-2 were observed in this paper. Commercial and original catalysts based on alumina and zeolite supports containing nanosized bimetallic active components of I, II, V-VIII groups have been tested in these reactions.

Experimental/methodology

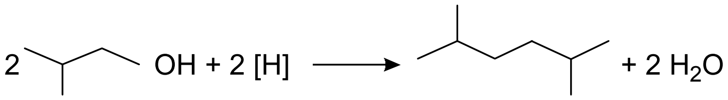
Industrial and laboratory elaborated catalyst samples were used in catalytic experiments. Both gaseous and liquid organic products in aqueous and organic phases were identified by GC-MS technique. The catalysts were tested in a PID Eng & Tech microcatalytic fixed-bed flow reactor unit and flow-circulated home installation set-up equipped with relevant instrumentation and control devices, under 250-450 °C, 5-100 atm of Ar and H_2, and substrates space velocity in the range of 0.6-1,5 h^{-1}. The local structure and charge state of active components were studied by XAS, XPS, XRD and TEM EDX. Relationships between structure of active components and catalytic activity of catalysts are discussed.

Results and discussion

Ethanol conversion to fraction of alkanes C_5-C_{10+}[1] at 300-350 °C in inert atmosphere was found to be catalyzed with industrial Pt/Al_2O_3 catalyst after special pre-activation as in (1):

$$mC_nH_{2n+1}OH + H_2 \xrightarrow[\text{were } n \geq 1;\ m \geq 2]{} C_{mn}H_{2mn+2} + mH_2O, \qquad (1)$$

2-methylpropanol-1 and 3-methylbutanol-1 were converted into 2,5-dimethyloctane and 2,7-dimethyldecane, respectively as in (2):



(2)

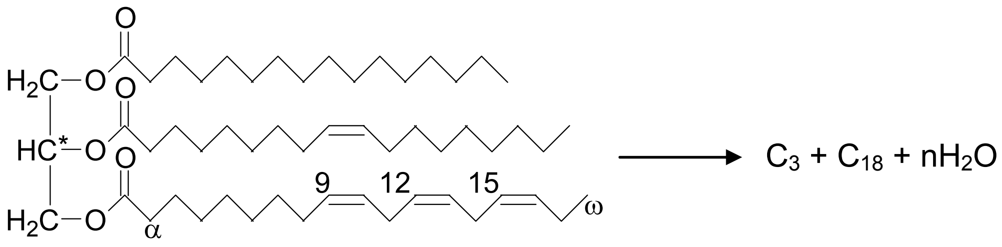
Cross-condensation of ethanol with acetone, bio alcohols, and glycerol in the presence of Pt/Al_2O_3 and [W(Ta)-Re]-catalytic systems leading toward the formation of new hydrocarbons with enlarged and branched carbon skeleton was observed (3):

$$C_2H_5OH + C_3H_5(OH)_3 \longrightarrow C_5\text{–}C_{12+} \text{ (alkanes, olefins)} + nH_2O \qquad (3)$$

Hydrogen consumed in product forming reactions 1-3 originated from in-situ in reaction zone via parallel reaction dehydrogenation and aromatization of initial alcohol.

Ethanol/bio-alcohols transformation is multivariate reaction and mainly depends on catalyst composition: 1) in the presence of modified platinum-contained catalyst reaction involves oligomerization of ethylene as intermediate; 2) aldol condensation is the main stage of hydrocarbons forming in the presence of W(Ta)-Re/Al_2O_3 and Pd-Zn/Al_2O_3 catalysts; 3) alkane-aromatic hydrocarbons forming according to well-known “hydrocarbon pool” mechanism[2] in the presence of Pd-Zn/ZSM-5 catalyst.

In the presence of original Pt-Sn/Al_2O_3 catalyst at 400-420 °C and 30 atm H_2 rapeseed oil was unexpectedly found to yield dominantly narrow alkane-olefins C_3, C_{18} and H_2O (4)[3]:

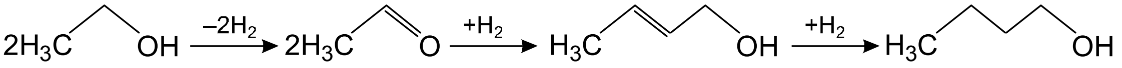


(4)

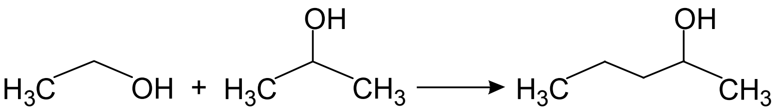
The total selectivity of direct deoxygenation reaches up to 99 %. The yield of C_3 and C_{18} hydrocarbons in the products was ~ 92 %. The total yield of C_1 and C_2 hydrocarbons as well as carbon oxides does not exceed 0,5-0,7 % that provides minimization of the carbon loss in the process of rapeseed oil deoxigenation.

Conversion of products fermentation and rapeseed oil into alkane-aromatic components of gasoline and kerosene without loading of molecular hydrogen was found. Hydrogen consumed for rapeseed oil hydrogenative deoxygenation was evolved in the reaction zone via coupled reaction carrying out of ethanol aromatization.

High activity (70 %) and selectivity (60-70 %) in reactions of β-alkylation of ethanol to n-butanol and cross-alkylation of ethanol by isopropanol-2 to iso-pentanol-2 was reached in the presence of nanosize bimetallic catalysts such as Au-Ni; Au-Cu and Au-Ag forming on the surface of γ-Al_2O_3 (5,6)^4.



(5)



(6)

Structure and evolution of the catalyst active sites were studied using TP-desorption of molecules-probes, XAFS, XPS, X-Ray and TEM HR.

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CATALYSIS FOR RENEWABLE RESOURCES: BIOALCOHOL CONVERSION

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The acid catalyzed conversion of bio-alcohols is of great interest for academia and industry as it involves complex catalytic reactions and offers a sustainable means for the production of renewable chemicals and fuels. Olefins produced by dehydration of bio-alcohols could serve as a building block for several essential compounds such as bio-based fuels and polymers. Nevertheless, development of a sustainable and energy efficient process largely depends on the design of a selective and active catalyst and requires an in-depth understanding of the catalytic reaction mechanism. This presentation focuses on fundamental mechanistic aspects of the zeolite catalyzed conversion of bio-alcohols and illustrates the effect of reaction conditions on competing reaction pathways.

Dispersion corrected periodic density functional theory (DFT-D2) calculations show that alcohol dehydration on Brønsted acid sites can occur via competing intramolecular and intermolecular reaction pathways [1,2,3] involving different elimination (i.e E1, syn- and anti-elimination) and substitution (SN1 and SN2) mechanisms [4] and allow to investigate the influence of zeolite acid strength and topology. DFT-derived energetics and vibrational analysis are used to obtain thermodynamic and kinetic parameters at relevant temperatures, which are fed to a microkinetic model. The first principles microkinetic modelling is validated by comparison to experimental data obtained in a broad range of reaction conditions. A systematic investigation of the effect of reaction conditions: reaction temperatures from 400 to 530 K, site time from 0 to 200 mol H+ s/mol alcohol, alcohol partial pressure from 0.1 to 1000 kPa and water to alcohol molar feed ratio from 1 to 40 mol/mol, on conversion and product selectivity is performed using microkinetic simulations. Reaction path analysis enables identification of rate limiting steps and reveals the crucial role of reaction conditions in determining the key surface species, dominant reaction mechanism and pathway.

PL-3

The difference in catalytic performance of the investigated zeolites is rationalized on the basis of differences in stabilization of the reaction intermediates and transition state structures within the zeolite framework. Such insights on the effect of zeolite topology on the reaction rates and product selectivity can provide guidelines for rational catalyst design.

Finally, a reactor model is applied to simulate a multi bed industrial scale adiabatic reactor, including relevant transport phenomena along with the complete reaction network.

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BIODIESEL AND HYDROCARBONS OBTAINED FROM WET ALGAL BIOMASS

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Proportion to the growth of energy consumption, increased pollution, making it necessary the development of "clean" energy sources that enable the stabilization of this situation of pollution. For this reason, the research has focused on developing new basic petrochemicals, renewable character, to produce fuels that can replace petroleum, which puts the biomass in an important role. In this sense, the incorporation of biodiesel energy matrix is a significant environmental gain due to the reduction of emissions. Being microalgae primary producers that store solar energy to convert it into biological energy [1-3].

The hydro-esterification process for the production of biodiesel from non-conventional raw material, such as microalgae biomass, proves to be a sustainable alternative – economically, environmentally, and ecologically – for substitution of petroleum derivatives (Diesel). Hydrolysis reaction of triglycerides (TG) consists of three stepwise forward and backward reactions as shown below. At each forward reaction step, one molecule of water is consumed producing one molecule of fatty acids (FA). For the backward reaction, on the other hand, G reacts with FA to return to MG. As in a similar manner, DG and MG also reverse to TG and diglycerides (DG), respectively, consuming one molecule of FA. TG + H_2O DG + FA DG + H_2O MG + FA MG + H_2O G + FA Methyl esterification of FA, shown below, is a major reaction to produce fatty acid methyl esters (FAME) whereas transesterification of TG is a major one in the conventional alkali- and acid-catalyzed methods. This esterification reaction is, therefore, an important step for high quality biodiesel fuel production. FA + MeOH FAME + H_2O [4-6].

Despite of growthing production in the USA and LatinAmerican countries like Argentina, Colombia and Brazil, there are some vehicle warranty restrictions for blending higher than B20 (20 % biodiesel/80 % fossil diesel). Renewable hydrocarbons obtained from lipids are a good alternative for larger diesel substitution and even to the emerging biojet industry as well as for green naphtha in the petrochemical sector. Hydrotreatment of triglycerides is a known process to obtain renewable hydrocarbons but investment cost is considerable higher than a conventional biodiesel plant. Moreover, hydrogen source and logistics are much more complex than methanol or any alcohol. Simultaneous hydrolysis and hydrogenation of fatty acids with hydrogen produced from glycerol liquid reforming in a single step using nickel catalysts has been described. In this work, palladium catalysts are presented in a lipid/water system where serial reaction involving hydrolysis, glycerol reforming, fatty acid hydrogenation (with no H_2 feeding) and finally, hydrodecarboxylation (HDC) of fatty acids producing 100 % green hydrocarbons from wet algae. An additional advantage here is that no drying step is necessary for the harvested algae. It can be used directly once water is mandatory for hydrolysis and reforming reactions [7-9].

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FUNDAMENTAL UNDERSTANDING OF ARTIFICIAL PHOTOSYNTHESIS FOR SOLAR FUEL PRODUCTION

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This lecture presents the research progress on solar fuel productions from artificial photosynthesis, namely photocatalysis and photoelectrocatalysis (PEC) processes with the emphasis on the fundamental understanding.

The great challenge of energy conversion photocatalysis lies in its complicated processes including light absorption (harvesting), charge separation and migration, and catalytic reactions. In order to gain high photon energy conversion efficiency, a photocatalyst or photocatalytic system must harmonically guarantee high efficiencies of all these three processes instead one of them. Semiconductors with appropriate phase junctions have been demonstrated to be an efficient approach for achieving efficient charge separation [1]. Cocatalysts play important roles in the assembly of efficient semiconductor photocatalyst. It has been conceptually demonstrated Pt-PdS/CdS dual cocatalyst system can achieve 93 % H_2 evolution activity in the presence of sacrificial reagents under visible light irradiation (λ>420 nm) [2,3]. Recently, it has been also demonstrated that electrons and holes can be spatially separated on the {010} and {110} facets of $BiVO_4$ crystal [4]. It has been demonstrated that the intrinsic nature of charge separation between different facets of $BiVO_4$ together with the synergetic effect of dual-cocatalysts plays key role in photocatalytic activity enhancement [5]. This work opens up a new avenue for the assembly of semiconductor crystal based artificial photosynthesis system by selectively loading of dual cocatalysts on the different facets.

Alternative approaches other than powdered semiconductor system should be also highly considered, such as photoelectrochemical (PEC) and solar cell coupled with water electrolysis catalyst systems. A Ta_3N_5 photoanode coated with ferrihydrite (Fh) layer on which Co_3O_4 water oxidation cocatalyst (Co_3O_4/Fh/Ta_3N_5) was deposited, could yield a photocurrent of 5.2 mAcm^{-2} at a potential of 1.23 V vs. RHE under AM 1.5G simulated sunlight irradiation. And remarkably, about 94 % of the initial activity could be maintained even after 6 h irradiation, which is due to the avoidance of the corrosion of Ta_3N_5 via. efficient hole storage and transfer by the Fh layer [6]. A self-biased photoelectrochemical–photovoltaic coupled system consisting of FeOOH/Mo:$BiVO_4$ photoanode and a Pt/p-Si solar-cell-based photocathode showed η_{STH} of 2.5 % under parallel irradiation [7].

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PL-6

CATALYSIS IN SYNTHESIS OF BIOMASS DERIVED PRODUCTS WITH PHYSIOLOGICAL PROPERTIES

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Cellulose, hemicelluloses, and lignin present in wood are typical non-food biomass and could serve as a source of chemicals. A lot of efforts in the last years were devoted to valorization of cellulose, hemicelluloses and lignin especially for generation of fuels. Besides cellulose, hemicellulose and lignin, lignocellullosic biomass contains a number of extractives.

In general, extractives from wood consist of several types of compounds, such as terpenes and terpenoids, fats and waxes, phenolic compounds and other substrates, for example alkanes and water-soluble compounds such as mono- and disaccharides. Industrially the most important wood-derived feedstock composed of extractives are tall oil and turpentine.

The potential of natural products as a source for new raw materials for fine chemicals, food components and/or other components beneficial for human wellness, via acting as models for synthetic approaches and catalytic transformations, is by far not exhausted. For example natural products and related drugs are used to treat 87 % of all categorized human diseases, acting as antibacterial, anticancer, anticoagulant, antiparasitic, and immunosuppressant agents, among others. In the lecture several examples would be considered.

One example is related to a pinene derivative (1*R*,2*R*,6*S*)-3-methyl-6-(prop-1-en-2-yl)cyclohex-3-ene-1,2-diol (diol in Figure 1) possessing potential anti-Parkinsonian activity. Parkinson's disease is one of the most common neurological diseases characterized mostly by motor disturbances. A range of catalysts have been applied for the synthesis of the target diol starting from verbenol oxide [1, 2].

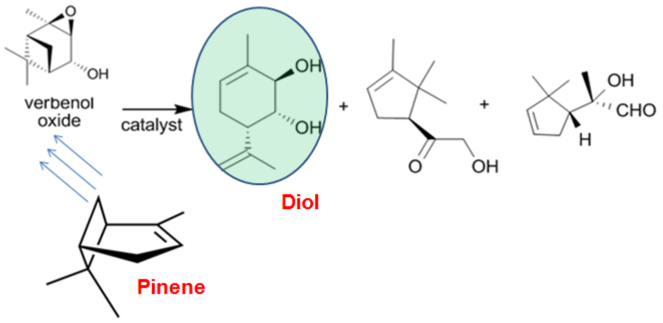

Figure 1. Synthesis of diol from pinene. Reaction steps include besides isomerization (shown) also other steps (not shown)

PL-6

Isomerisation of verbenol oxide to cyclopentyl and cyclohexyl compounds taking place with iron modified zeolites happens in parallel to formation of a dioxinol compound, (2*S*,4a*R*,8*R*,8a*R*)-4,4,7-trimethyl-2-phenyl-4a,5,8,8a-tetrahydro-4*H*-benzo[d][1,3]dioxin-8-ol, exhibiting analgesic activity, when verbenol oxide is condensed with (substituted) benzaldehyde (Figure 2).

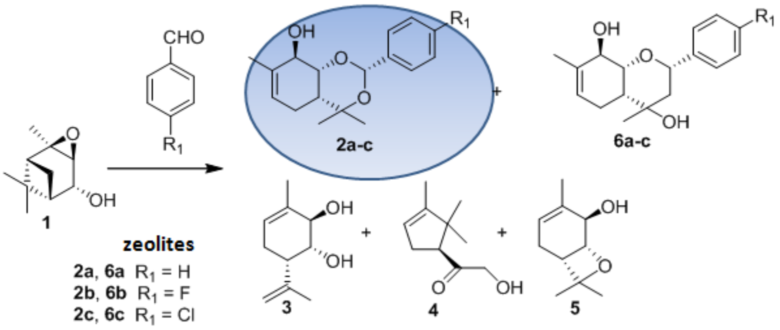

Figure 2. Synthesis of dioxinol by reaction of verbenol oxide with benzaldehyde

Different parent zeolites as well as their metal modified forms and mesoporous materials were employed in the comparative investigation [4]. In the lecture it would be shown how activity and selectivity of the tested catalysts can be correlated with their physico-chemical properties.

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KEYNOTE LECTURES

KL-1

SYNTHESIS OF *O*-ISOPROPYLIDENE DERIVATIVES FROM SUGARS USING SULFONIC ACID FUNCTIONALIZED SILICA CATALYSTS

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Sulfonic acid functionalized ordered mesoporous silica (OMS-RSO_3H) materials are a new class of inorganic porous solid acid catalysts with stronger acidic strength, greater stability and reusability [1]. A series of sulfonic acid-functionalized ordered mesoporous silica (RSO_3H-OMS), such as RSO_3H-MCM-41and RSO_3H-SBA-15, were prepared by post-synthesis grafting method *via* oxidation of thiol-functionalized silica (RSH-OMS) [2]. All the prepared materials were systematically characterized using various analytical, spectroscopic and imaging techniques, viz., XRD, TEM, XRF, BET, FT-IR and ^{29}Si MAS-NMR. In order to establish the nature of acid sites in the functionalized materials, NH_3-TPD studies were performed. A better understanding on the generation of different acid sites is provided by NH_3-TPD and ^{29}Si MAS-NMR studies which depends on condensation of sulfonic groups with silanols. This, in-turn, rely on sulfonic acid loading.

Acetonation of sugars is an important reaction that protects 1,2-diols of sugars as *O*-isopropylidene derivatives (acetonides) which is critical in multi-step syntheses in organic, medicinal, and carbohydrate chemistry [3]. The RSO_3H-OMS catalysts were tested for synthesis of *O*-isopropylidene derivatives of sugars *via* acetonation reaction and their activity is compared with sulfonic acid-functionalized silica-gel (RSO_3H-SG) prepared in a similar manner. Various sugars, viz., *D*-glucose, *D*-galactose, *D*-xylose and *D*-mannitol of different chain lengths and structures, were investigated for acetonation reaction with selectivity towards di-*O*-isopropylidene derivatives in presence of RSO_3H-OMS catalysts. Table 1 summarized the reaction results. In the liquid-phase acetonation of sugars, all the catalysts yield selectively di-*O*-isopropylidenes as the main product owing to the presence of strong acidic sites. It can also be seen from this table that *O*-isopropylidene derivatives of different sugars were prepared with excellent yield within 1-3 *h* in a simple work-up process. In addition, the RSO_3H-OMS catalysts retained their high activity even after recycling in comparison to RSO_3H-SG.

Table 1. Acetonation of various sugars by RSO_3H-OMS catalysts[a]

Sugar	Product	time (*h*)	Yield (*wt.%*)[b]		
			RSO_3H-SG	RSO_3H-MCM-41	RSO_3H-SBA-15
D-Glucose	1,2:5,6-Di-*O*-isoproylidene-α-*D*-glucofuranose	3	49.4 (83.6)	85.9 (99.8)	71.1 (98.3)
	1,2:5,6-Di-*O*-isoproylidene-α-*D*-glucofuranose[c]	3	45.1 (80.5)	84.1 (99.0)	71.0 (98.2)
D-Galactose	1,2:3,4-Di-*O*-isopropylidene-α-*D*- galactopyranose	1	85.0 (100)	88.0 (100)	95.0 (100)
D-Xylose[d]	1,2:3,5-Di-*O*-isopropylidene-α-*D*-xylofuranose	0.5	60.0 (98.9)	89.0 (100)	93.0 (100)
D-Mannitol	1,2:3,4:5,6-Tri-*O*-isoproylidene-*D*-mannitol	1	82.0 (92.0)	84.0 (100)	71.0 (100)

[a] Reaction conditions: Catalyst = 50 *mg*; sugars = 500 *mg*; dryacetone = 30 *ml*; 2,2-DMP = 2 *ml*; 60 °*C*; N_2 atm. [b] Conversion is given in parenthesis. [c] Using recycled catalysts. [d] At room temperature.

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CATALYSIS TO PRODUCE CHEMICAL SUPPLIES FROM RENEWABLE SOURCES

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The production of industrial chemical supplies from renewable sources is a challenge that involves concepts of green chemistry and sustainability[1,2] and, in this context, oleochemistry play an important role. In the coatings industry, alkyd resins synthesized from polyols, dibasic acids and fatty acids exhibit good performance properties that make them one of the most used materials in this field and represents a very good example of polymer obtained from renewable source[3]. Alkyd film formation on a substrate occurs via a series of chemical reactions involved in oxidative polymerization, also called oxidative curing or drying. In this work, the oxidative polymerization of linseed oil, which was used as a model alkyd resin, was investigated in the presence of cobalt(II), manganese(II) and iron(II) 2-ethylhexanoate and complexes obtained by modifying these metal carboxylates with chelating nitrogen ligands (phenanthroline family)[4]. Catalysts based on Sn(IV) were tested in esterification and transesterification reaction in the presence of methanol and ethanol. Several parameters (reaction time, temperature, and catalyst amount) were systematically evaluated. All complexes were active in simultaneous esterification/transesterification reactions. The results obtained and discussed in this work can help the development of new catalytic systems to biodiesel production from oils with very high acid content [5].

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KL-3

EFFICIENT CATALYTIC DEPOLYMERIZATION OF LIGNIN IN SUPERCRITICAL ETHANOL

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Obtaining renewable fuels and chemicals from lignin presents an important challenge to the use of lignocellulosic biomass to meet sustainability and energy goals. With cellulosic ethanol production approaching commercial practice, it becomes necessary to valorize side-streams such as lignin.

We developed a thermocatalytic process for the depolymerization of lignin in supercritical ethanol; this process delivers high yields of mainly alkylated mono-aromatics (60-86 %, depending on the lignin used) with a significant degree of deoxygenation. The oxygen-free aromatics can be used to replace reformate or can serve as base aromatic chemicals; the oxygenated aromatics may be useful as low-sooting diesel fuel additives or as building blocks for polymers.

The monomers obtained via thermal cracking of lignin are protected from repolymerization by alkylation of aromatic rings and phenolic hydroxyl groups with ethanol. The capping reactions hinder undesired repolymerization reactions of phenolic fragments, with formaldehyde originating from the starting lignin. These assertions will be supported by model and real feed studies showing how alkylation of various functional groups protects the monomers from repolymerizing. In addition to its role as a capping agent and hydrogen source, ethanol also scavenges formaldehyde. This explains why the use ethanol is significantly more effective in producing monomers and avoiding char than the use of methanol. We will discuss the properties of the versatile catalyst based on abundant metals to drive these reactions. The mechanistic insights provide new impetus for the design of better processes to valorize lignin.

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"PHYSICAL" CATALYSIS OF CHEMICAL REACTIONS UNDER THE INFLUENCE OF EXTERNAL ELECTRIC FIELDS. HDTV AND SHF IN CATALYSIS

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The author considered the theoretical foundations and experimental results of catalytic processes under the action of the selective absorption of the electromagnetic field of SHF and HDTV.

The conditions of the effective absorption of the field and its transformation in the temperature gradients, the nature and characteristics of the radiation as well as of the absorbing materials (magnetic susceptibility, ohmic resistance and frequency characteristics of the field) are analysed. The methods for application of fields, the experimental techniques and the technological solutions have been considered.

The experimental results are centred around two main processes:

1) Pyrolytic reactions of biomass and organic waste,

2) Functionalization of nanoparticles and of creation on this basis of enzyme-like catalysts – nanoenzymes.

The pyrolytic conversion of biomass and organic waste into liquid and gaseous fuel. The author analyze the demand for (need for) pyrolytic processes, resources and feedstock for pyrolysis technologies in terms of conversion of biomass of technological and municipal waste. A qualitatively new approach to the problem – pyrolysis in variable temperature fields – has been considered. Kinetic regularities of the process have been studied and a number of mathematic models have been analyzed. The optimal conditions for conversion of organic materials into liquid fuel have been found. The setups of continuous action have been created and the conversion into fuel of polymers (polyethylene, polypropylene, polyethylene terephthalate), microscopic algae biomass, heavy hydrocarbons and tar, activated sludge treatment plants refineries has been experimentally studied.

Functionalization of nanoparticles – creation of nanoenzymes. The methods for polymerization of monomers to form a polymer coating on the surface of nanoparticles in the field of microwave radiation. Under the influence of an external electromagnetic field, the conditions "hot" particles are realized. – A variation of

KL-4

amino acid composition was used to obtain the functionalized nanoparticles having a high catalytic activity in the reactions of the pyrolysis of polysaccharides, starch and cellulose.

Their characteristics and kinetics of processes have been studied. Under consideration are the problems of obtaining new composite materials under the action of the "physical" catalysis in SHF and HDTV energomagnetic fields.

FOSSIL AND BIO CARBON FATE IN FCC CO-REFINING

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In order to meet the international renewable energy targets by 2020 (up to 10 % share in all forms of transportation fuels), a realistic alternative to the first generation bio-fuels is to produce hybrid bio- and fossil fuels by co-refining biomass pyrolysis oil with crude oil fractions in a conventional oil refinery. However, co-refining may lead to changes in products quality, such as a higher aromaticity, residual oxygenates in the hybrid gasoline and higher coke deposits during the FCC cracking step. A detailed understanding is required on how the oxygenated moieties introduced in the added bio-oils affect the cracking mechanism and how both fossil and renewable carbon are distributed among the FCC products. In this study carried on a micro activity test (MAT) reactor, up-graded pyrolysis bio-oils are added to crude oil distillates (VGO type) to undergo the FCC cracking/regeneration cycle by using model or industrial FCC catalysts. The quality of the produced "hybrid" FCC fuels is analyzed and compared, focusing on coke generation and nature as a signature of the cracking process, in tight relationship with catalysts structure and active sites accessibility. Other strategies for hybrid fuels synthesis (hydro-treating) will be briefly discussed as well.

KL-6

NANOCOMPOSITE CATALYSTS OF BIOFUELS TRANSFORMATION INTO SYNGAS: DESIGN, REACTION MECHANISM AND PERFORMANCE

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Transformation of biofuels into syngas via steam/oxysteam reforming is now considered as one of the most important task of catalysis in the energy-related fields. Due to a high reactivity of oxygenates a heavy coking is observed leading to the catalyst deactivation. To deal with this phenomenon, active components comprised of complex oxides with a high lattice oxygen mobility (favors efficient gasification of coke precursors) promoted by Ni/Co-based alloys (responsible for oxygenates activation) are suggested. For achieving a high performance in these reactions, monolithic substrates with a good thermal conductivity are promising for providing an efficient heat supply to the catalyst and prevent emergence of cool/hot zones deteriorating performance.

This work reviews results of extensive research aimed at design and characterization of such nanocomposite structured catalysts performance in transformation of a variety of biofuels (ethanol, acetone, ethyl acetate, anisole, glycerol, turpentine, sunflower oil) [1-4]. Next basic problems are considered:

1. Atomic-scale factors controlling oxygen mobility and reactivity in complex oxides with perovskite (LnMnCrO), fluorite (PrCeZrO) and spinel (MnCrO) structures (both bulk and loaded on high surface area Mg-alumina, $CaTiO_3$, tialite), their acid/base properties and features of strong interaction with supported metal/alloy nanoparticles (Ni, Co, Ni+Pt, Ni+Ru, etc).
2. Effect of the active component composition, specificity of surface sites and nature of oxidant on basic mechanistic features of biofuels (mainly, ethanol) transformation into syngas as elucidated by a complex of transient methods (*in situ* FTIRS, isotope and chemical transients, pulse microcalorimetry).
3. Design of structured catalysts by supporting optimized active components on heat-conducting substrates (Ni-Al foams, Fe-Cr-alloy corrugated foils, gauzes and microchannel platelets with protective corundum layers, microchannel cermets, SiC monolithic substrates with porous walls, etc).

4. Structured catalysts performance in pilot-scale reactors operating on real concentrated feeds and its mathematical modeling.

For steady-state optimized nanocomposite active components high mobility and reactivity of strongly bound surface oxygen (heat of adsorption 500-600 kJ/mol O_2) provides realization of step-wise redox mechanism of biofuels transformation with the rate determining stage corresponding to the rupture of C-C bond in activated fuel molecule on the metal site (Ni-Ru alloy nanoparticle, etc) facilitated by the interaction with oxygen species at the metal-support interface.

Optimized structured catalysts provide a high yield of hydrogen (H_2 content up to 50 %) in the IT range both in steam and autothermal reforming of biofuels at short contact times. Main by-product is CH_4 due to cracking, while for alumina-supported active components C_2H_4 is formed on acid sites. Suppressing acidity by increasing Mg loading and O_2 addition to the feed decreases C_2H_4 content, thus suppressing coking, stable performance was confirmed for more than 100 h time-on-stream. For heat-conducting substrates (Ni-Al foam, microchannel platelets etc.) mathematical modeling demonstrated the absence of any heat- and mass-transfer effects. No spallation or cracking of the active components on metallic substrates was revealed.

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ORAL PRESENTATIONS

Section I. CATALYSIS IN DENDROCHEMISTRY FOR VALUABLES PRODUCTION

Catalytic systems for hemicellulose depolymerization

Catalytic processing of tall oil and tar, Selective conversion of sugars

Catalytic transformations of CO_2 to fine chemicals

ONE-POT DIRECT CONVERSION OF BIOMASS CELLULOSE INTO C_3 AND C_4 OLEFINS OVER Pt/H-USY ZEOLITE CATALYST

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Introduction

Renewable resources are attracting increasing attention as substitutes for fossil resources. Among them, biomass cellulose offers numerous advantages as a ubiquitous feedstock. Recently, the direct conversion of cellulose into hydrocarbons using solid catalysts under pressurized hydrogen has been reported [1-3]. Under the pressurized hydrogen atmosphere, although celllulose conversion and paraffin yields were high, no olefins were formed. We have reported an one-pot direct conversion of cellulose to C_3 and C_4 hydrocarbons over Pt/H-zeolite catalysts at 443 K under hydrothermal conditions without hydrogen [4,5]. Results revealed that the activity and selectivity were affected by the zeolite structure, the SiO_2/Al_2O_3 ratio, and the supported state of Pt. However, the olefin selectivity was still low.

Therefore, to increase the olefin selectivity, we investigated the effects exerted on the cellulose conversion and product selectivities by the catalyst pretreatment and the reaction time. The fine structure of supported Pt particle on the USY zeolite was characterized using TEM and EXAFS.

Experimental

Pt/H-USY catalysts were prepared by the ion-exchange method; 1 wt % Pt was supported on H-USY(14) (Tosoh Corp.) zeolite, with the number in parenthesis representing the SiO_2/Al_2O_3 ratio. Tetraammineplatinum(II) nitrate was used as the precursor of supported Pt. The obtained powder was calcined at 803 K for 8 h in air flow. Before the catalytic reaction, the catalyst was pre-treated in a fix-bed contiuous-flow glass reactor with 10 % H_2 gas or air flow at 773 K for 1 h.

Catalytic reaction were performed in a batchwise autoclave (30 mL, SUS 316). Cellulose powder (microcrystalline, MP Biomedicals Inc.) was pre-treated using a planetary ball mill to produce fine particles. Reaction conditions are follows; catalyst: 0.25 g, cellulose: 0.25 g (8330 C-μmol), water: 20 mL, temperature: 443 K, reaction time: 1–24 h, Ar atmosphere. The reaction products were analyzed by GC-FID, GC-TCD, TOC, and HPLC.

Results and discussion

To increase olefin selectivity, the effect of pretreatment of Pt/H-USY(14) catalyst on its activity and selectivity were investigated. Figure 1 presents C_3+C_4 yield and selectivity in the cellulose conversion over H_2-reduced or air-oxidized Pt/H-USY(14) catalysts at 443 K for 3 h. The air-oxidized Pt/H-USY(14) catalyst exhibited higher C_3+C_4 olefin selectivity (39.7 C-%) than the H_2-reduced catalyst did (0.1 C-%), although the C_3+C_4 hydrocarbon yields were slightly low. Results revealed that the olefin selectivity was influenced greatly by the catalyst pre-treatment condition.

To clarify the difference of olefin selectivity, the fine structure of supported Pt was assessed using XAFS measurement. Pt L_3-edge EXAFS spectra after Fourier transformation for H_2-reduced or air-oxidized Pt/H-USY(14) catalyst are shown in Figure 2. Only Pt-Pt bond was observed over the H_2-reduced Pt/H-USY(14) catalyst. However, both Pt-Pt and Pt-O bonds were observed over the air-oxidized Pt/H-USY(14) catalyst, which indicated that the supported Pt was partially oxidized. These results suggest that the oxidized Pt (PtO_x) species might be effective for olefin formations.

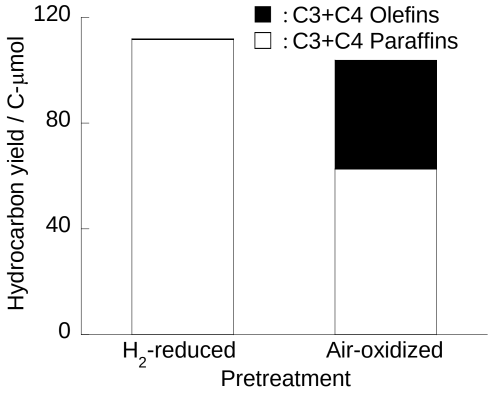

Fig. 1. The C_3+C_4 yields over H_2-reduced or air-oxidized Pt/H-USY(14) catalyst

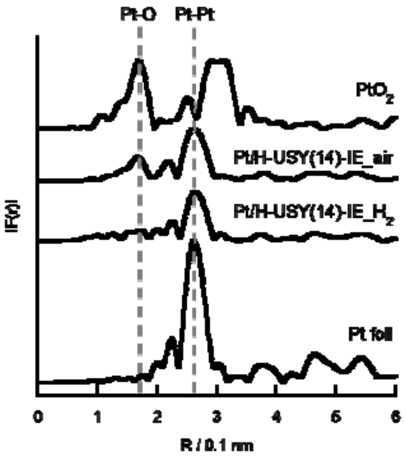

Fig. 2. Pt L_3-edge EXAFS spectra of H_2-reduced or air-oxidized Pt/H-USY(14)

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MECHANO-CATALYTIC DEPOLYMERIZATION AS A TOOL FOR LIGNOCELLULOSIC BIOMASS FRACTIONATION: A WAY TO CONVERSION INTO FUELS AND CHEMICALS

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The utilization of lignocellulosic plant biomass has gained increased research attention in the past decade as shown a great potential to contribute in the decreasing dependence on the use of fossil fuel resources as well as in the depletion of greenhouse gases. Unfortunately, the main roadblock for the direct conversion of this renewable carbon source is the complex nature of the plant biomass in which cellulose, hemicellulose and lignin form a complex and recalcitrant structure that is very difficult and costly to depolymerize [1]. To date, depolymerisation technologies such as steam explosion, pre-hydrolysis with acid or alkaline solutions, among others, have been widely investigated [2]. On the other hand, all these pre-treatments processes have shortcomings such as large energy input, lack of selectivity, solvent stability and recycling. These drawbacks currently raise the price of reactive biomass component to an unacceptable level for use on a large scale in bio-refinery; therefore, innovation is expected to make the process economical attractive.

In this presentation, we discuss an innovative mechano-catalytic process developed at our Centre that involve combination of acid impregnation in aqueous media and ball milling to depolymerize cellulose and plant biomass. In the case of cellulose, it was found that water soluble oligomers were produced when milling in presence of various acids, with sulphuric acid being the most effective in producing water soluble oligosaccharides fraction. Rapid depolymerisation of cellulose was proportional to acid concentration and milling time. Soluble fractions were found to have a degree of polymerization of less than 10 monomer units that were primarily linked via $\beta(1\rightarrow4)$ glycoside bonds along with $\alpha(1\rightarrow6)$ linkages. On the contrary, when plant biomass such as bagasse and rice hulls was used, the increase in solubility of biomass was not proportional to increase in acid amount. Maximum solubility of biomass was obtained at optimum acid concentrations (Figure 1).

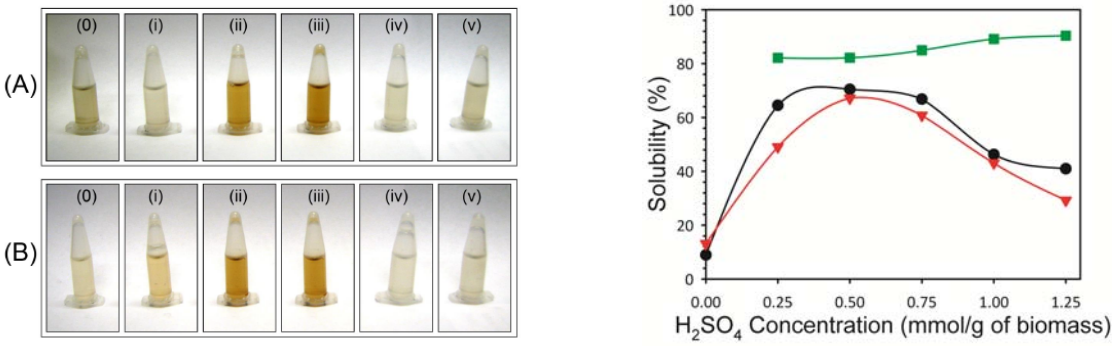

Figure1: Solubility of biomass after mechano-catalytic pretreatment.
Black line: Bagasse (A) and Red line: Rice hulls (B). Green is bagasse milled under argon

Condensation of soluble matter was observed at higher acid amounts which were influenced by presence of air during milling. Replacing air with Ar eliminated the condensation of soluble products and highest solubility of 90.2 % of biomass was achieved with 1.25 mmols of acid per g of biomass. Figure 2 shows a scheme for the depolymerisation process.

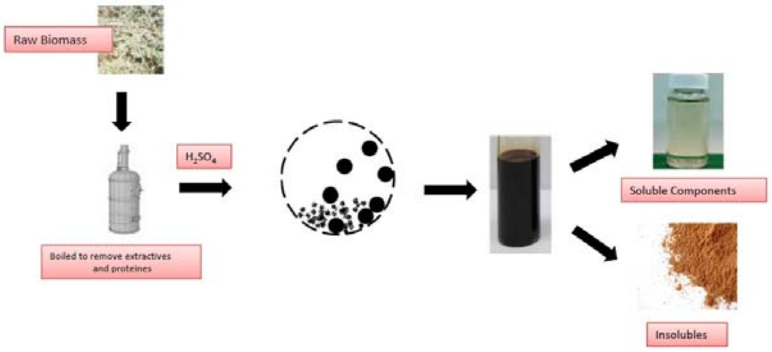

Figure 2: Scheme for mechanocatalytic depolymerisation of biomass

Then the cellulose oligomers in liquid state were catalytically tested using metal Ni and Ru supported catalyst on a batch reactor and ultimately a plug flow catalytic reactor. It was found that, catalytic reaction of bagasse pre-treated with 0.75 mmols of H_2SO_4 per g under air resulted in 29.3 % yield of sugar alcohols (21.2 % xylitol, 8.1 % hexitol). Some examples on catalytic conversion of cellulose into sugar alcohols and furanic compounds as well as lignin fraction into phenols and aromatics are also presented here as prove for the potential downstream processing of the soluble biomass fractionation.

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HYDROLYTIC HYDROGENATION OF CELLULOSE TO SUGAR ALCOHOLS: EFFECT OF CATALYST TYPE, REACTION CONDITIONS & NATURE OF CELLULOSE

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Cellulose is one of the most abundant forms of biomass on the earth, and the last few decades the transformation of cellulose to fuels and chemicals has attracted the research interest. Cellulose is a polysaccharide consisting of a linear chain of several hundred to many thousands of $\beta(1\rightarrow4)$ linked D-glucose units. Hydrolytic cleavage of the β-1,4-glycosidic bonds between two anhydroglucose units is of fundamental interest and plays an essential role in cellulose processing, as this degradation step paves the way for other catalytic transformations [1]. The hydrolysis of cellulose produces glucose, which is a versatile precursor to fuels, plastics, pharmaceuticals, and other value-added chemicals. The hydrolysis of cellulose requries an acidic castalyst or it can be done enzymatically. Amongst the various solid catalysts studied, those based on carbons have been widely used, mainly in the form of acidic sulfonated microporous or mesoporous carbons (e.g. AC-SO_3H, CMK-3-SO_3H) [2,3]. Once glucose is produced then it can be selectively hydrogenated to to sorbitol, a platform chemical with many uses, on supported Ni or Ru catalysts. In addition to the two step process, several bifunctional catalytic systems have been developed for the simple, one-step transformation of cellulose into sorbitol and other sugar alcohols. Such systems comprise either a liquid acid and a supported metal catalysts or even more challenging only hydrogenating metals supported on acidic substrates.

The present study aims to a systematic investigation of the performance of supported noble metals (i.e., Pt and Ru) on various types of carbons (micro/mesoporous & mesoporous) in the hydrolytic hydrogenation of commercial microcrystalline cellulose, ball-milled amorphous cellulose, and cellulose recovered from lignocellulosic (wood) biomass after various hydrolysis and extraction pretreatments. Particularly, more emphasis was placed on the effect of metal content (1-5 %), the method of metal pretreatment/reduction (H_2 at 350 °C or $NaBH_4$), the effect of reaction time (3-24 hrs), the effect of hydrogen pressure, while catalyst regenaration was also investigated. The hydrolysis/hydrogenation experiments were carried out in a batch autoclave stirred reactor under relatively low hydrogen pressure (2.0 MPa) at 150-200 °C and various times. The physicochemical characterization of the catalysts was performed by ICP-AES, Boehm titration, N_2 sorption, TEM, XRD, XPS, etc. The reaction products determined by using GC-MS and HPLC analysis.

Both metals (Pt, Ru) were highly dispersed on the surface of activated carbon (AC), even at relatively high loadings (ca. 5 wt. %), as can be seem in the TEM images of Fig. 1.

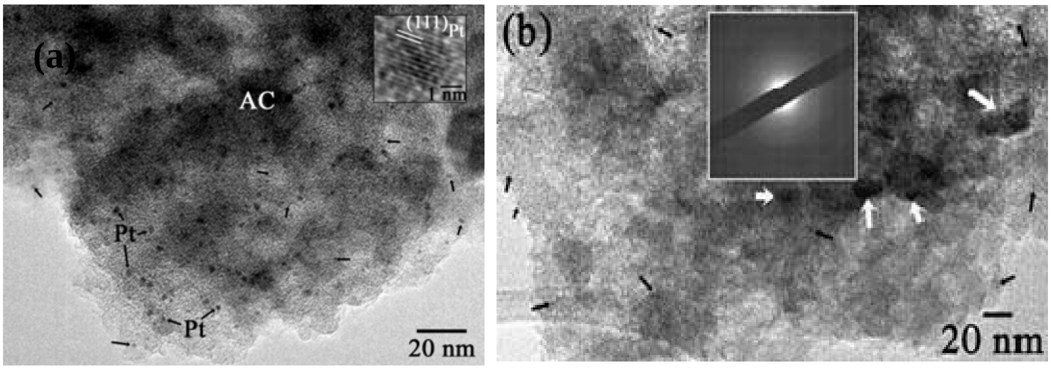

Figure 1. TEM images of (a) 3 % Pt/AC-H and (b) 5 % Ru/AC-B catalyst on activated carbon (AC)

Significant variations in activity and product selectivity were observed, depending on the type and content of the metal (Ru or Pt), the nature of the support (acidic or neutral carbon surface) and the reaction conditions. The Pt and Ru/AC catalysts, especially Pt, were highly active and selective in cellulose hydrogenation towards sorbitol, regardless the method of catalyst activation (reduction). Their performance in the hydrolytic hydrogenation of cellulose was dependent on relative rates of cellulose hydrolysis to glucose and the subsequent hydrogenation/hydrogenolysis of glucose to sorbitol and various smaller alcohols, such as PG/EG, glycerol, threitol, etc. In general, it was shown that the Pt based catalysts are more selective towards sorbitol while the Ru catalysts leads also to the formation of smaller sugar alcohols. The crystallinity of cellulose was also very important and determined the rate of its hydrolysis to glucose.

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LEWIS-ACID CATALYSED ORGANOSOLV LIGNIN EXTRACTION FROM WHEAT STRAW

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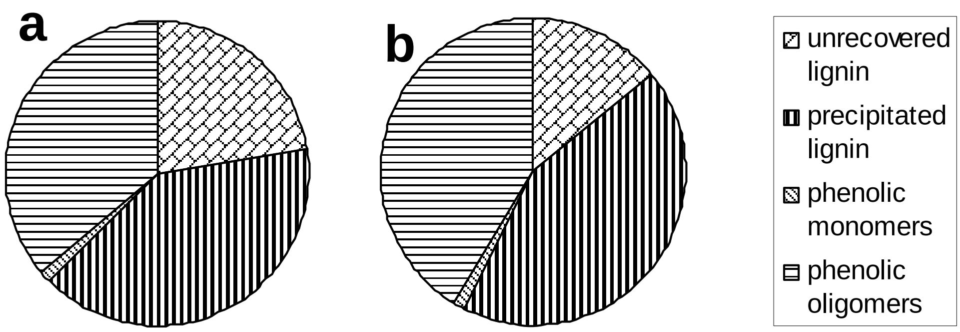
The recovery of lignin-derived phenolic products by fractionation of lignocellulosic biomass is a promising way to replace high-value added oil-derived products by specialties issued from renewable resources. Catalytic control of the fractionation of biomass is the ideal tool to achieve the selectivities needed for economically sustainable processes.

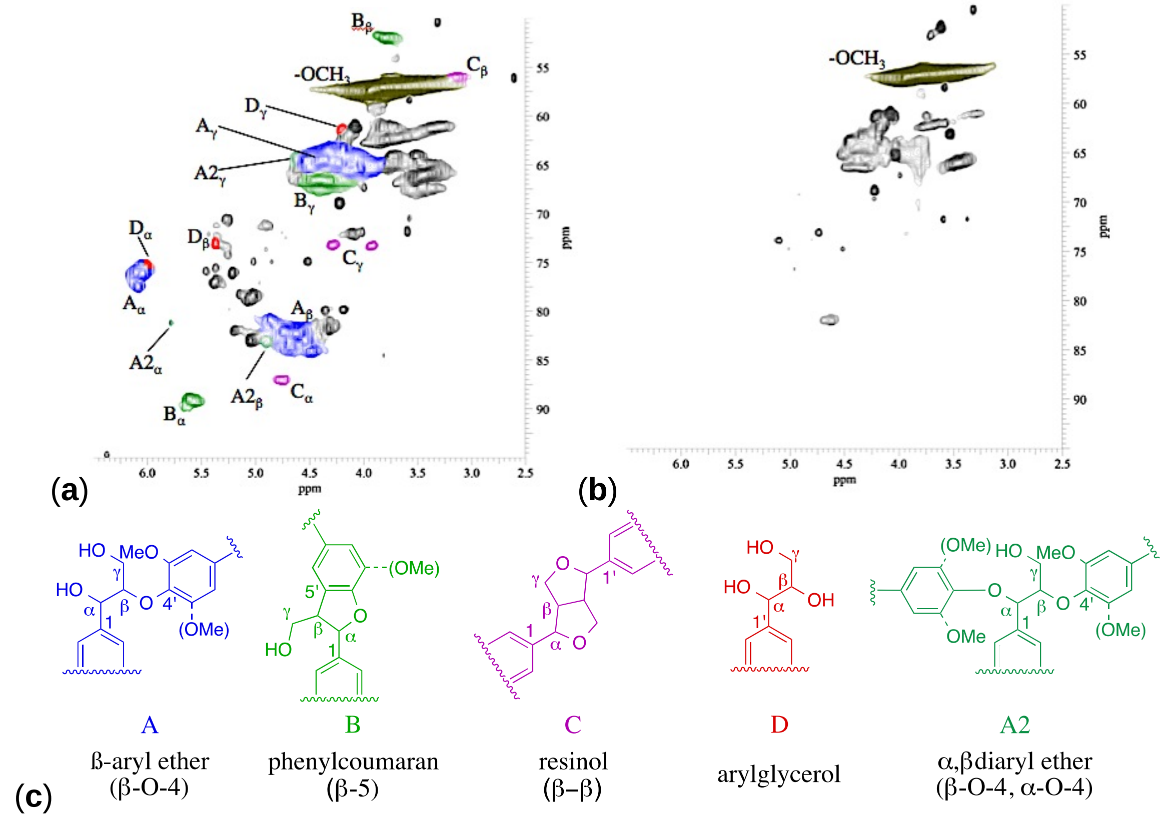
In this project, Lewis acids have been studied as catalysts in the organosolv treatment of wheat straw. Fractionation of the lignocellulosic biomass and fragmentation of lignin have been performed in aqueous ethanol in the presence of $FeCl_2$, $CuCl_2$, $FeCl_3$, $Ga(OTf)_3$, $ZrOCl_2$ or $Sc(OTf)_3$ [1]. The lignins were characterised in terms of molecular weight, β-O-4 linkage content and chemical functions through size exclusion chromatography, thioacidolysis, ^{31}P and ^{13}C NMR and FT-IR spectroscopies.



Selectivity of delignification of wheat straw at 160 °C in 66 % aqueous ethanol in the presence of 8 mmol/L Lewis acids with cation hardness (a) <10 and (b) >20 eV

The degree of delignification and the yield of precipitated Klason lignin increased with the hardness of the Lewis acid. About half of the delignification products were water-soluble monomers and oligomers. Phenolic oligomers were targeted as intermediates in polymer chemistry.

The precipitated lignins were significantly different from the parent lignin in straw and their properties were tailored by the choice of the Lewis acid. The molecular mass, the amount of OH groups and of aliphatic C-O bonds decreased as the hardness of the acid cation increased. The hardest Lewis acids produced condensed, g-units enriched and aryl ether linkage-free lignins with molecular mass lower than 6 KDa. The control of the properties of lignin is especially appealing for the elaboration of additives for the textural control of suspensions.



^{1}H-^{13}C HSQC NMR spectra (aliphatic region, δ_C/δ_H 45-95/2.5-6.5, ppm) of (**a**) H_2SO_4 issued lignin and (**b**) $Sc(OTf)_3$ issued lignin and (**c**) aryl ether linkages found herein

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NOTE ON THE USE OF THE ACID VALUE FOR FOLLOWING THE HYDROLYSIS OF TRIOLEIN BY IMMOBILIZED LIPASE

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The trioelin is largely found in edible oils (peanut, palm, olive and soya), being an important source of di and monolein, which, in turn, are employed as emulsifiers, emollients and texturing agents in a variety of pharmaceutical, cosmetic and food products [1-2]. Mono and diolein are obtained by controlled glycerolysis of triolein under conditions such as 700 psi, 220 °C/225 °C and in presence of inorganic catalyst (for example, $Ca(OH)_2$) [3]. Besides the difficulty on stopping the hydrolysis at desired moment, the reaction mixture must be redistilled in order to remove undesirable by-products formed due to the harsh reaction condition used. An alternative would be the use of immobilized lipase – which can be recovered at the end of reaction, minimizing the cost of the enzyme regarding to the overall cost of the process – which requires mild reaction conditions and do not generate environmental unfriendly compounds. The purpose of this study was to evaluate the possibility of using the acid value determination – a reliable, cheap and simple analytical method, which could be disposed and handled near the reactor in operation – in order to control the triolein hydrolysis.

Lipozyme® (30U/g) and trioelin (purity 65 %; AV = 0.75 mg NaOH/g) were purchased from SIGMA®. All of the other chemicals used were of the highest analytical grade. The hydrolysis was carried out in a 500 mL batch reactor fed with 300 mL of 0.01 M phosphate buffer (pH 7.4) in which were suspended triolein (0.05 M or 0.2 M) and Lipozyme (10 % w/w regarding to the initial amount of triolein). The reaction was followed for 3 h or 6 h and the temperature set at 40 °C, 50 °C or 60 °C. After the reaction, the acid value (AV) of the medium was determined by titration with 0.1 M NaOH according to the AOCS Official Method [4].

The results are presented in Table 1. It can be seen that the acid value (AV) indicates that the intensity of hydrolysis depended on the triolein initial concentration, reaction time and temperature. The highest triolein hydrolysis occurred for 6 h of reaction at 50 °C and 0.2 M triolein. Figure 1 shows, clearly, that the pair (temperature/reaction time) affects sharply the hydrolysis of triolein, being (50 °C/6 h) the best one. Finally, by setting the triolein concentration at 0.2 M we observed that the AV decreased 23 % and 27 %, respectively, when the temperature of the reaction was changed from 50 °C to 60 °C either for 3 h or 6 h reaction time (Table 1).

Table 1. Acid value (AV), expressed as mg NaOH/g of sample, for the triolein hydrolysis by Lipozyme carried out at different temperatures, initial substrate concentrations and reaction times

TRIOLEIN (M)	TEMPERATURE (°C)	REACTION TIME 3 h	6 h
0.05	40	1.12	1.31
	50	5.02	3.74
	60	5.51	3.81
0.2	40	2.18	2.10
	50	28.63	38.75
	60	22.12	28.25

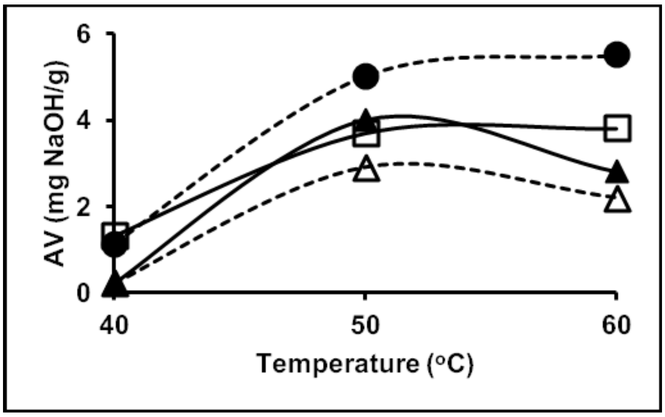

Figure 1. Variation of the acid value (AV) against temperature at reaction time of 3h (…) and 6h (–). **Triolein 0.05M:** 3h (•); 6h (□); **Triolein 0.2M** [multiply AV by 10]: 3h (Δ); 6h (▲)

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Acknowledgements

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COMPARISON OF CATALYTIC AND PHOTOCATALYTIC WATER OXIDATION MATERIALS THROUGH THE REACTION KINETICS IN A THREE-PHASES BUBBLING REACTOR

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There is an ever-increasing necessity in the society for energy resources which are cost effective and sustainable. Researchers all over the world are investigating photochemical water splitting (WS) to H_2 and O_2, as a promising way to store solar energy. A widely studied approach to the make light-driven WS reaction consists in separating the functions of light harvesting and conversion from fuel-forming catalysis. Different metal oxides (containing Ir, Co, Ru, Ni, Rh and Mn) have been studied as heterogeneous and homogeneous catalysts to carry out the four electron oxidation of water to O_2 under photochemical conditions. As this is concerned, Cobalt has emerged as the most versatile non-noble metal for the development of synthetic H_2- and O_2-evolving catalysts. Such catalysts can be coupled with photosensitizers to generate photocatalytic systems for the water oxidation half reaction (the most challenging one), or to produce directly light-induced hydrogen from water[1]. Other systems based on manganese oxides (MnOx) have also shown good activities[2], with the advantage of being earth abundant and cheap materials. Alternative to these systems are semiconductor photocatalyst, due to their cost effectiveness and stability. Among them, $BiVO_4$ and WO_3 have attracted a high interest for this application because of their good photocatalytic activity for the water oxidation (WO) reaction, low band gap, abundance and not-toxic components.

Particulate photocatalytic systems are frequently used to study the half reactions of water splitting for H_2 or O_2 evolution in the presence of sacrificial reagents. This type of study has the advantage of being much simpler and less expensive to develop and use than photoelectrochemical cells, as well as it is particularly suited to determine whether or not a given catalyst satisfies the kinetic and thermodynamic requirements for the water splitting reaction[1]. Batch reactors are generally used for this purpose. In such systems cumulative O_2 or H_2 evolution data is discontinuously analyzed versus time. Recently, we developed a reactor system and a mathematical model to investigate the kinetics of O_2 evolution, with a high precision. Fig. 1 illustrates the reactor designed and implemented to measure O_2 evolution, into which Ar flows at a constant rate and bubbles into the continuously stirred liquid phase. The oxygen concentration in the outgoing gas mixture is measured through a micro gas chromatograph. Thus, the actual oxygen flow and cumulative O_2 production are determined. Coupled with the information on the O_2 dissolved in the liquid phase (measured with a Clark-type electrode), we have developed a comprehensive mathematical model (based on O_2 formation at the catalyst surface, then diffusion at the dispersed gas bubble interface, and finally mixing with the stagnant gas in the pocket on the top of the liquid surface), able to retrieve the actual O_2 evolution reaction rate (RO_2) from the recorded data, in order to study the chemical kinetics of different photocatalytic system. This methodology have been employed in our laboratories to study several catalysts and photocatalysts (*e.g.* Co- and Mn-oxides, as well as $BiVO_4$ and WO_3) [2,3,4,5], in order to retrieve their intrinsic activity for the WO reaction under visible light irradiation.

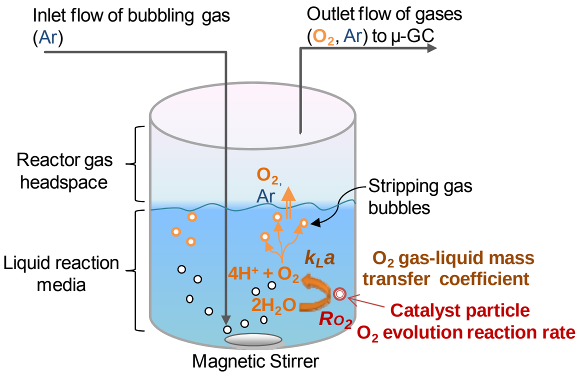

Figure 1: Sketch of the bubbling reactor

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CATALYTIC DEPOLYMERIZATION OF HEMICELLULOSES AS AN IMPORTANT STEP OF BIRCH-WOOD BIOMASS COMPLEX PROCESSING INTO VALUABLE CHEMICALS

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Acid-catalytic depolymerization of hemicelluloses is used for obtaining xylose and other valuable products from xylose. Besides, the removal of hemicelluloses from wood can increase the efficiency of lignocellulose biomass further processing into valuable chemicals (e.g. microcrystalline cellulose (MCC), glucose and bioethanol).

In Russia the birch-wood, containing around 28-30 % of hemicelluloses is the most widely available source of raw material for xylose production. To ensure selective depolymerization of hemicelluloses to xylose the optimum conditions of birch-wood hydrolytic conversion should be selected which allow to minimize the transformation of other wood components to side products.

This report summarizes the results of study of birch-wood hemicelluloses depolymerization in the processes of xylose obtaining with the use of acid catalysts, of cellulose and glucose obtaining by wood “explosive” autohydrolysis and by wood catalytic delignification with H_2O_2.

Acid-catalyzed hydrolysis of birch-wood

The activity of soluble and solid acid catalysts (H_2SO_4, acid-modified SBA-15 and carbon Sibunit, Amberlyst, Naffion) was compared in hydrolysis of birch-wood chemicelluloses to xylose at mild conditions (temperature 100 °C, atmospheric pressure). The maximum yield of xylose (77 % mas. from the initial content of hemicelluloses in wood) was obtained by birch-wood prehydrolysis in the presence of 2 % and 3 % H_2SO_4. Solid acid catalysts have a reasonable activity only at temperature 150 °C.

Activation of a birch-wood water suspension in grinding mills with different designs results in variation of wood structure, chemical composition and increases by 2-3 times the rate of the process of hemicelluloses acid-catalyzed hydrolysis.

“Explosive” autohydrolysis of birch-wood

From the main components of birch-wood biomass the hemicelluloses are the most sensitive to short treatment by water steam at temperatures 187-240 °C and pressures

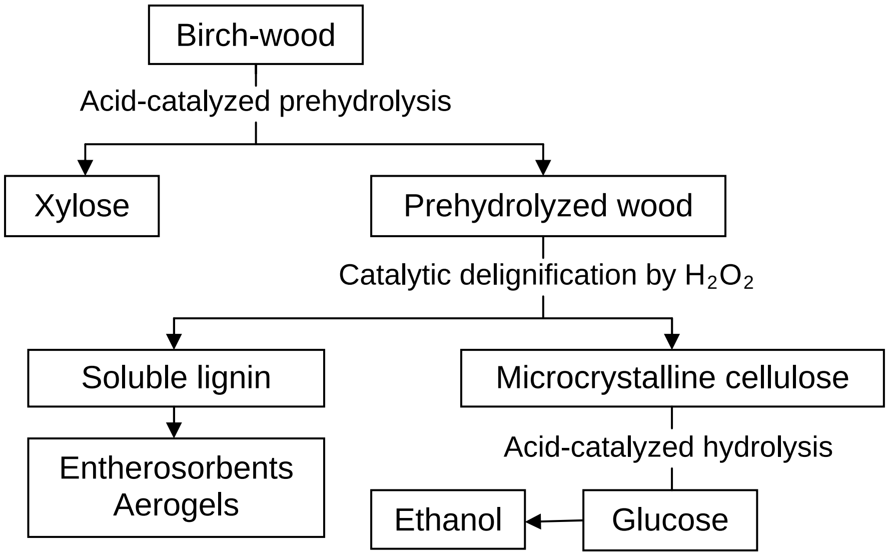
1.2-1.3 MPa. They are completely hydrolyzed at temperatures higher 220 °C, whereas the cellulose and lignin are rather stable at these conditions of treatment. Water-soluble compounds obtained in "explosive" autohydrolysid process contain along with C_5 and C_6-sugars, low-molecular weight lignin, acetic acid, furfural and in the minor amounts, methanol, isopropanol, propionic acid, hydroxymethylfurfural.

Catalytic delignification of birch-wood by hydrogen peroxide

The treatment of birch-wood by mixture "H_2O_2–CH_3COOH–H_2O–catalyst TiO_2" at temperatures 70-100 °C makes possible to combine the depolymerization of lignin, hemicelluloses, amorphous part of cellulose and to produce microcrystalline cellulose by one-step process. It was difficult to remove completely hemicelluloses and even after birch-wood catalytic delignification at 100 °C during 4 hours the obtained MCC contain near 5.5 % mas. of hemicelluloses, obviously co-crystallized with cellulose. MCC samples that not contain lignin and hemicelluloses were obtained by combination of steps of birch-wood "explosive" autohydrolysis and futher oxidative catalytic delignification of cellulose product with H_2O_2.

Complex processing of birch-wood biomass

Based on optimized method of hemicelluloses removal from birch-wood the integrated processing of main wood biomass components with obtaining xylose, MCC, glucose, bioethanol from polysaccharides and sorption materials from lignin (entherosorbents, organic and carbon aerogels) was suggested.



Scheme of birch-wood complex processing

Acknowledgements

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POLYOXOMETALATE-SUPPORTED Ru NANOPARTICLES FOR SELECTIVE CONVERSIONS OF XYLAN INTO PENTITOLS

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Xylan (hemicellulose) is the second most abundant polysaccharide after the cellulose. Agricultural wastes (crop, sugar wastes etc.) contain up to 35 wt. % of xylan, hardwood – 20-25 wt. %, softwood – 7-12 wt. %. The hydrolysis of the xylan in the presence of acid catalysts gives xylose, which can be hydrogenated over metal catalysts to xylitol – a valuable natural sweetener, anticaries, and anti-inflammatory agent, as well as raw material for the production of surfactants, ethers, synthetic resins etc. Xylan hydrolysis byproducts are: lyxose – xylose isomer; furfural – a product of the dehydration of the xylose and lyxose. Consequently, a one-pot hydrolytic hydrogenation over bifunctional catalysts containing both acidic and redox catalytic sites would allow to avoid the formation of these products and to increase the yield of xylitol. The only example of the hydrolytic hydrogenation of hemicelluloses over bifunctional catalysts described in [1], wherein the catalyst 5% Ru/MCM-48 was applied for processing of arabinogallactan to polyalcohols (total obtained yield was 30 mol. %).

The aim of this work was the development of bifunctional catalysts for the one-pot hydrolytic hydrogenation of the xylan on the basis of Cs salts of heteropolyacids (acid site) containing Ru nanoparticles (redox site).

Cs salts of heteropolyacids: $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$ и $H_4PMo_{11}VO_{40}$ were prepared according methods described in [2]. Their stability under hydrothermal conditions was tested at 180 °C. $Cs_2HPW_{12}O_{40}$ и $Cs_3HSiW_{12}O_{40}$ salts appeared to be the most stable.

3 % $Ru/Cs_2HPW_{12}O_{40}$ and 3 % $Ru/Cs_3HSiW_{12}O_{40}$ were prepared by the wetness impregnation method using aqueous solution of $Ru(NO)(NO_3)_3$ as the ruthenium precursor and CsHPA as the support followed by reduction of the ruthenium precursor in a stream of hydrogen at 300 °C. The catalysts were characterized by the N_2 absorption, XRD, FTIR, HREM. Catalysts were tested in the one-pot hydrolytic hydronenation of xylan at 180 °C and 5 MPa (H_2). Concentration

of the substrate and the catalyst were 10 g/L Reaction mixture was analysed by HPLC.

The results of catalitic tests are given in the Table 1. The main products of the one-pot process over the both catalysts are: the target polyols – xylitol and arabitol; the intermediate – xylose. The side product – furfural was observed only in the presence of 3 % Ru/$Cs_3HSiW_{12}O_{40}$ catalyst. The yields of these products, as well as the total yield pass through a maximum at 2-3 hours. Further, total yields decrease.

3 % Ru/$Cs_3HSiW_{12}O_{40}$ catalyst appeared to be more active than 3 % Ru/$Cs_2HPW_{12}O_{40}$ though less selective toward to formation of xylitol. This fact may be due to the greater acidity of $Cs_3HSiW_{12}O_{40}$ salt which accelerate the reactions of the hydrolysis, isomerization and dehydration leading to formation of xylose, lyxose and furfural, respectively. While the reaction rate in the hydrogenation of xylose to xylitol does not change. However, the rate of reaction, and hence the selectivity and the total one-pot process may be increased by increasing the hydrogen pressure.

Table 1. Catalytic perfomance of the 3 % Ru/$Cs_2HPW_{12}O_{40}$ and 3 % Ru/$Cs_3HSiW_{12}O_{40}$ in the one-pot hydrolytic hydronenation of xylan

Catalyst	CA*, mol/(h·g)	Total products yield, %	Time	Xylitol		Arabitol		Xylose		Furfural	
				S**, %	Y***, %	S, %	Y, %	S, %	Y, %	S, %	Y, %
3 % Ru/ $Cs_2HPW_{12}O_{40}$	3.56	68.1	3	90.0	60.6	9.4	6.4	3.5	2.4	0.0	0.0
3 % Ru/ $Cs_3HSiW_{12}O_{40}$	5.92	96.8	2	69.6	67.4	18.0	12.5	13.1	12.7	3.8	3.7

*CA – catalytic activity per gramm of catalyst; **S – selectivity; ***Y – yields.

Thus, the catalysts allowing to obtain polyols with the high yields (67 % for 3 % Ru/$Cs_2HPW_{12}O_{40}$ and 80 % for 3% Ru/$Cs_3HSiW_{12}O_{40}$) by the one-pot hydrolytic hydrogenation of the xylan were developed.

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BIOBASED BUILDING BLOCKS FROM 5-HYDROXYMETHYLFURFURAL

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5-hydroxymethylfurfural (HMF) was identified by the U.S. Department of Energy (DOE) [1] as one of the top ten bio-based platform chemicals with significant market potential [2]. The molecule, which is derived from the C6 sugar fraction of lignocellulosic biomass, may undergo several chemical transformations to valuable chemicals and fuels. For example, it can be oxidized to 2,5-diformylfuran (DFF) as well as furan 2,5-dicarboxylic acid (FDCA) to provide building blocks for the polymer industry. It can also be reduced to 2,5-furandimethanol (FDM) or biofuel additive 2,5-dimethylfuran (DMF).

FDM has been identified as useful building block in the synthesis of interesting biopolymers [3]. In this study, we report on a tunable and highly selective catalytic systems for the conversion of HMF to either 2,5-furandimethanol (FDM) or 2,5-dimethylfuran (DMF). These include novel copper-doped porous metal oxides in combination with biocompatible ethanol as solvent, mild reaction temperatures (100-220 °C) and relatively low H_2 pressure are applied. In addition, the use of noble-metal-free copper-zinc nano-alloys will be reported for both the synthesis of FDM as well as for the saturated analog of FDM, 2,5-dimethyltetrahydrofuran, and 2,5-dimethylfuran (DMF) with combined product yields up to 97 % (200-220 °C, 20-30 bar H_2).

Identification of reaction intermediates formed during the reduction processes and their evolution in time will be discussed and a reaction network will be provided.

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Ni-MODIFIED Mo CARBIDE CATALYSTS FOR HYDRODEOXYGENATION OF BIOMASS-DERIVED MODEL COMPOUNDS

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In recent years, transition metal carbides, in particular molybdenum carbide, have attracted much attention due to their catalytic properties, that are similar to those of noble metals in a variety of reactions such as hydrocarbon hydrogenation and isomerization, hydrodesulfurization, hydrodenitrogenation etc [1]. In addition to the transition metals carbides ability to adsorb and activate hydrogen, these materials are mechanically, chemically and thermally stable which made them the potential catalysts for hydroprocessing of such an aggressive feedstock as pyrolysis oil. According to literary data, the introduction of nickel to Mo carbide has the significant effect on the catalytic activity and selectivity in methane dry reforming [2], dibenzothiophene HSD [3], CO hydrogenation [4]. The objective of the present study was to evaluate the catalytic performance of the Ni–Mo-C catalysts with various Ni/Mo ratios in hydrotreating of renewable feedstock model compounds. The reactions of anisole and ethyl caprate hydrogenation was carried out at 320° C and a hydrogen pressure of 6 MPa in a batch reactor. The samples were prepared by the thermal decomposition of metal precursors with citric acid and ethyl silicate followed by high-temperature hydrogen treatment. According to XRD data, the formation of β-Mo_2C, Ni_6Mo_6C carbides and the metallic Ni was observed; the amounts of each phase depend on Ni/Mo ratio in the catalysts. The main reaction products of ethyl caprate hydrotreatment was C10 saturated hydrocarbon and decyl alcohol, that indicates the predominance of hydrogenation route without decarboxylation. The increase of Ni/Mo ratio in the samples result in higher selectivity towards the decane formation. Ni-modified sample with the highest Ni_6Mo_6C phase content was more active in ethyl caprate hydrotreatment than monometallic Mo carbide catalyst. The results of Ni-Mo-C catalytic performance in anisole hydrotreatment study indicate that Ni addition suppresses the direct deoxygenation without hydrogenation of the aromatic ring and enhance the other reaction route - hydrogenation of the benzene ring without oxygen removal.

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OP-I-11

SELECTIVE CONVERSION OF FURFURAL TO METHYLFURAN OVER Mg/Fe/O MIXED OXIDE USING METHANOL AS H TRANSFER REACTANT

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The hydrogenation of furfural (FU) towards furfuryl alcohol (FAL) and 2-methylfuran (MFU) is a key step in the up-grading of biomass-derived furanic compounds. Several catalytic systems have been studied to perform furfural hydrogenation using molecular hydrogen[1,2]. However, these reactions are not entirely green, requiring high-pressure and expensive costs associated to the process. Recently efforts have been made in the catalytic transfer hydrogenation using alcohol as H-donor in liquid phase[3,4]. Nevertheless, the development of a continuous catalytic process, using non-noble metals, for the production of FAL and MFU, is still an attractive topic.

In our previous work, MgO catalyst has been found to be an excellent catalyst for liquid phase reduction of FU to FAL using methanol as H-donor[5]. Hereby, we report a Fe/Mg/O catalytic system in gas phase reduction of FU towards MFU.

In order to optimize the catalyst preparation strategy, different synthesis approaches were adopted including impregnation (FeOx/MgO_1_10) and co-precipitation (Fe/Mg/O_1_10). With the aim of finding the effect of Fe dopant, comparable reactions over pure Fe_2O_3, Fe_3O_4 and physical mixed Fe_2O_3/MgO and Fe_3O_4/MgO were also carried out. Results were summarized in Figure 1; all the catalysts have been prepared with the same metal molar ratio (1Fe/10Mg). Notably, the only target product MFU can be obtained over the impregnated catalyst (FeOx/MgO_1_10). The Physical mixture of either Fe_2O_3/MgO_1_10 or Fe_3O_4/MgO_1_10 exhibited a slight change in the products distribution, still producing a high amount of MFU, especially, high yield of MFU can be obtained over Fe_3O_4/MgO_1_10. On the contrary, pure iron oxides (Fe_2O_3 and Fe_3O_4) exhibited high furfural conversion and less FAL residues, but higher carbon loss was also presented. It suggests that the acidity origin from Fe phase will dramatic impact furanic compounds degradation. These catalytic studies suggests that the hydrogenolysis of FAL towards MFU is greatly influenced by the nature of Fe phase, namely redox features and acid-base properties. In addition, the co-precipitation system (Fe/Mg/O_1_10) led to inferior results, revealing that beside Fe percentage, thus proper location of Fe phase is also important for MFU formation.

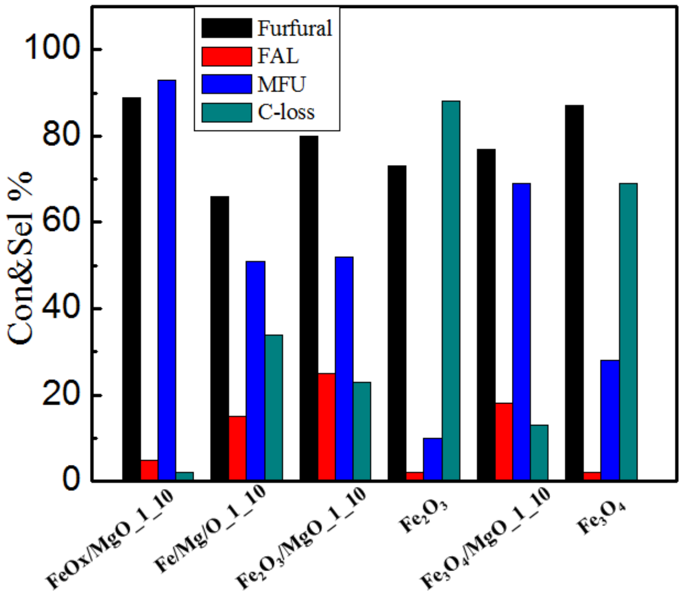

Figure 1. Catalytic performance of furfural hydrogenation over different Fe/Mg/O based catalysts (the molar ratio Fe/Mg was fixed at 1/10) – Reaction conditions: T = 380 °C for 1 hour, atmospheric pressure. Residence time 1.1 s. Methanol/furfural = 10/1 molar ratio, rest N_2

In conclusion, obtained results highlight the potential application of H-transfer reaction over Mg/Fe/O based catalyst, bypassing the need for high pressure hydrogenation using noble metal catalysts, as an efficient process for the selective de-oxygenation of biomass derived molecules. It is obvious that Fe doping greatly promotes the FAL hydrogenolysis by increasing H-transfer ability from methanol.

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OP-I-12

ONE-STEP PRODUCTION OF γ-VALEROLACTONE FROM FURFURAL IN THE PRESENCE OF ZrO_2-GRAFTED SBA-15

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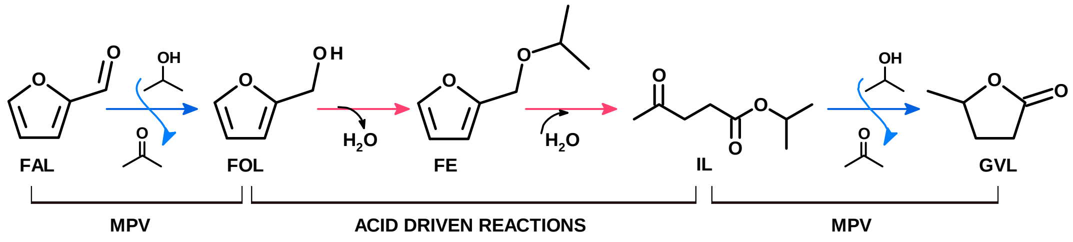
Biomass derived γ-valerolactone (GVL) is an important platform molecule which finds application as green solvent or as starting material for the production of green fuels and polymers [1]. GVL production from furfural can be achieved through a series of transformations involving of carbonyl reductions and acid driven transformations (Scheme 1). This cascade of reactions could be accomplished by using catalysts with activity in both types of chemical reactions, catalyst such as zirconium functionalized silicas which display Lewis acidity and H-transfer capability through Meerwein-Ponndorf-Verley transformations [2]. Within the present work we demonstrate the feasibility of this chemical route from furfural to GVL in a single step, by using isopropanol as sacrificing alcohol and SBA-15-supported ZrO_2 as catalyst.



Scheme 1. GVL production from furfural by a cascade reaction. FAL, furfural; FOL, furfuryl alcohol; FE, Furfuryl-isopropyl ether; IL, isopropyl levulinate; GVL, γ-valerolactone

Experimental

ZrO_2 was grafted onto mesostructured silica (SBA-15) by post-synthesis functionalization [3]. In order to obtain different Zr loadings and surface coverage, the process was repeated up to 3 times. Catalytic experiments were performed in liquid phase in a stainless-steel stirred autoclave.

Results

Figure 1 shows the obtained product yields at different temperatures for the three tested catalysts (1, 2, or 3 ZrO_2 grafted equivalent layers). The activity of all the catalysts seemed to be quite temperature-sensitive, yielding furfuryl alcohol as unique product at 90 °C. Under these conditions, a direct relationship between Zr loading and H-transfer activity was clearly observed, corroborating the crucial role of the tested materials in this starting transformation. However, producing the rest of the intermediates in the sequence from FAL to GVL required of higher temperatures. Thus, FE was only observed upon increasing the reaction temperature to 130 °C, whereas IL was only detected above 150 °C. The last transformations (from IL of GVL), was only produced at significant levels at 170 °C, when IL was produced in a high extent. This is probably due to the weak acidity of the ZrO_2-based materials which requires of higher reaction temperatures to promote the difficult transformation from FE to IL (supposedly to be the rate-determining stage in the formation of GVL from FAL). The catalyst prepared with two equivalent layers of ZrO_2 over SBA-15 [ZrO_2-SBA-15 (2)] seems to have the appropriate combination of properties (acid loading and accessible MPV-active zirconium sites) to promote the overall reactions cascade, involving MPV and acid-driven transformations. In this way, ZrO_2-SBA-15 (2) sample is able to produce a maximum molar GVL yield close to 40 % after 6 hours of reaction starting from furfural. Further assays involving the optimization of the catalyst properties for the maximization of GVL production are being investigated.

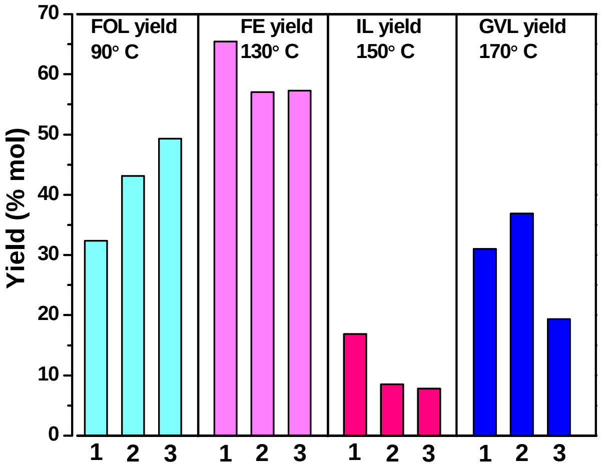


Figure 1. Molar products yield as a function of Zr content. Reaction conditions: t_r: 6 h; 2-propanol:FAL molar ratio, 50:1; FAL:catalyst mass ratio, 2.5:1.

Conclusions

GVL production from furfural in one-step was accomplished balancing reaction temperature and Zr loading of the ZrO_2 grafted SBA-15 catalyst.

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OP-I-13

CONVERSION OF BIOGAS TO SYNTHESIS GAS OVER NICKELCONTAINING CATALYSTS

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Time in just more than a century humanity has developed, mastered and continues to intensively develop various direction of thermal, hydro and nuclear power, which have become the traditional industries. The energy consumption in the world increases continuously and accordingly leads to the permanent decline available of fuel reserves in the crust. The pace of global growth of the production of electricity is 3-4 times higher than the rate of population growth in the world. To relatively of global growth, being sought to alternative feedstocks for producing fuel. In the industrial scale produced liquid fuel from coal by catalytic processing of synthesis gas obtained by coal gasification. By the possible supplementary and partial replacement of traditional types of fuel is the producing and use of biogas, as a significant its amount of formed at bacterial fermentation of biomass plant and animal origin, also in the process of processing of organic raw materials. An important argument in favor of this energy source is the need to solve at the present level of environmental problems associated with waste disposal and, first of all greenhouse gases. This subject is given huge attention in the European Strategic Plan of Energy Technology (SET), which establishes a new agenda for scientific research in the field of energy to significantly reduce the greenhouse gas (GG) emissions in 2020. Extensive resources, high profitability of production make biogas most promising source of hydrocarbons capable of providing current and future needs of mankind in the energy and hydrocarbon feedstock. The composition of biogas depends on the process parameters, composition and type of feedstock. The main components of biogas produced in anaerobic bioreactors: methane (CH_4) and carbon dioxide (CO_2), as impurities, can be contain hydrogen sulfide (H_2S), ammonia (NH_3), hydrogen (H_2), nitrogen (N_2), carbon monoxide (CO) and oxygen (O_2). Biogas produced in this manner may be converted into synthesis gas by steam reforming or dry reforming using corresponding of catalysts. The relevance of this paper is due to involvement of methane and carbon dioxide – two greenhouse gases in the process of producing synthesis gas. The synthesis gas, in its turn, raw material for obtaining a number of commercial products by means industrially-applicable of GTL-technology.

In this paper NiLa/Al_2O_3 catalyst was synthesized and investigated carbon dioxide conversion of biogas. Experiments to test the efficiency of the catalysts were carried out using an automated flow catalytic device (FCD-1). The amounts of the reaction products were determined by chromatograph (Chromos-1000).

Conversion of biogas were investigated in the temperature range of 600-850 °C, at the atmospheric pressure and the ratio of reactant was CH_4:CO_2 = 2:1. The results are shown in Figure 1.

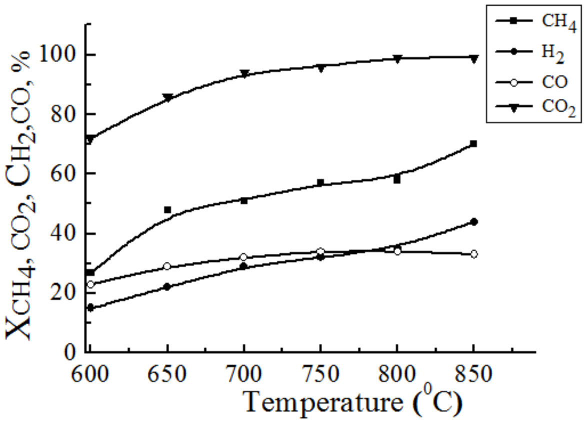

Figure 1. Effect of reaction temperature on the conversion of gases (CH_4, CO_2) and concentration of the reaction products

With increasing reaction temperature, conversion of methane and dioxide carbon increased too. Thus degree of conversion of methane increases from 28 to 67 % when increased reaction temperature from 600 to 850 °C, also conversion of carbon dioxide is increased from 69 to 96 % under the same conditions. All the tasting temperature range of 750-800 °C the dry reforming of biogas produced synthesis gas with ratio of 1:1.

OP-I-14

RATIONAL DESIGN OF HIGHLY STABLE AND SELECTIVE $Zn_xZr_yO_z$ CATALYST FOR DIRECT CONVERSION OF BIOMASS-DERIVED OXYGENATES TO OLEFINS

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With increases in availability and decreases in its production cost, biomass derived oxygenates such as ethanol have become an attractive platform molecule for the production of value-added chemicals [1]. Infrastructure is already in place to produce ethanol from renewable biomass for gasoline blending. With limits on ethanol levels in gasoline blending, favorable economic conditions for ethanol as a feedstock are expected. Isobutene (IB) is a highly valued industrial chemical that can be used as solvents, fuel additives, and precursors for synthetic rubber. In order to become less dependent on finite fossil fuel resources, sources other than crude oil are needed for isobutene.

Mixed metal oxides are promising catalysts due to their dual acid-base functionality for multi-sequential step reactions converting ethanol to IB. For ethanol to IB (ETIB), acetone, formed via acetaldehyde ketonization, has been identified as a key intermediate. We have previously reported that basic sites are needed for acetaldehyde and acetone formation [2]. We have also found that both Lewis acid-base pairs and Brønsted acid sites [3] are active for aldol-condensation of acetone at < 100 °C. At temperatures higher than 350 °C, only Brønsted sites were found to be selective to IB. In our previous work, IB yield as high as 83 % from bio-ethanol was achieved over $Zn_xZr_yO_z$ catalysts [2]. Further work revealed that weak Brønsted acid sites were responsible for increased IB yield [3]. However, the $Zn_xZr_yO_z$ catalyst prepared by a hard template method ($Zn_xZr_yO_z$) suffered from deactivation and also produced undesired C4 isomers with the IB stream due to the presence of Brønsted sites. To mitigate these two issues, a new catalyst ($Zn_xZr_yO_z$-I) with only Lewis sites was designed and synthesized. In this presentation, steady state and kinetic experiments, and pyridine-infrared spectroscopy (Py-IR) have been used to correlate the acidic sites with activity of $Zn_xZr_yO_z$ catalysts. Insight has been provided on which reaction steps are catalyzed by Brønsted and Lewis acidic sites. By pinpointing the difference between and role of each type of acidity in ethanol conversion, higher selectivities of the desired IB can be achieved and fundamental understanding of acidic site requirement can be applied to the rational design of catalysts for selective conversion of other bio-derived compounds.

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OP-I-15

AQUEOUS PHASE REFORMING OF C_5 AND C_6 SUGARS AND SUGAR ALCOHOLS

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The aqueous phase reforming (APR) is a single step and low temperature (≤250 °C) energy efficient process, that produces hydrogen from water-diluted oxygenated hydrocarbons obtained directly from biomass degradation. In effect, the production of H_2 by APR is ruled by important selectivity challenges: the mixture of H_2 and CO_2 formed in the process is thermo-dynamically unstable at low temperatures with respect to the formation of methane (methanation) or other light alkanes. Initial work from the Dumesic group [1] pointed to the ability of supported platinum catalysts to produce hydrogen with good selectivity; on the other hand, the APR process can be also designed to favor the formation of heavier alkanes, that is not necessarily a secondary goal of the entire process of renewable resources exploitation.

In this research work, aqueous solutions of D-(+)-Glucose (100 g/L, Sigma-Aldrich), D-Sorbitol (≥98%, Sigma-Aldrich), D-(+)-Xylose (≥98%, Sigma-Aldrich) and D-(+)-Xylitol (≥98%, Sigma-Aldrich) were investigated. The initial concentrations of these saccharides and their alcols were 1 wt % (10g/L) for all the tests carried out. The catalysts for this reaction were 5 wt % Pt on γ-alumina powder. A 300-mL stainless steel Parr batch reactor, equipped with magnetic driven stirrer and temperature controller system, was used for the APR tests. It was outfitted with a gas collector at the outlet for micro-GC analysis. In a typical experiment 10 mL of substrate were diluted until 100 mL (1 wt %) and 0.25 g of Pt/Al_2O_3 powder were put inside the reactor with a previous mixing. After securing the reactor head, nitrogen gas was allowed to flow through the reactor and to purge out air from the headspace. The reactor was then pressurized up to a definite value of N_2 (from 1 to 6.5 bar), sealed, and then heated to a certain temperature (for most experiments, at 225 °C). The reaction was allowed to run for several reaction times, from 1 to 24 h. Sampling of the gas phase was carried out at the end of this phase. The amount of H_2, O_2, N_2, CO and CH_4 were analyzed using a SRA MyGC (molsieve 5A column), while CO_2, C_2H_6 and C_3H_8 were also quantified in the micro GC (PPU column). Both columns are connected with a TCD. The liquid byproducts of the reaction were collected and analyzed with a high performance liquid chromatograph (HPLC) and two different detectors: a refractive index detector (RID) and a photoionization detector (UV).

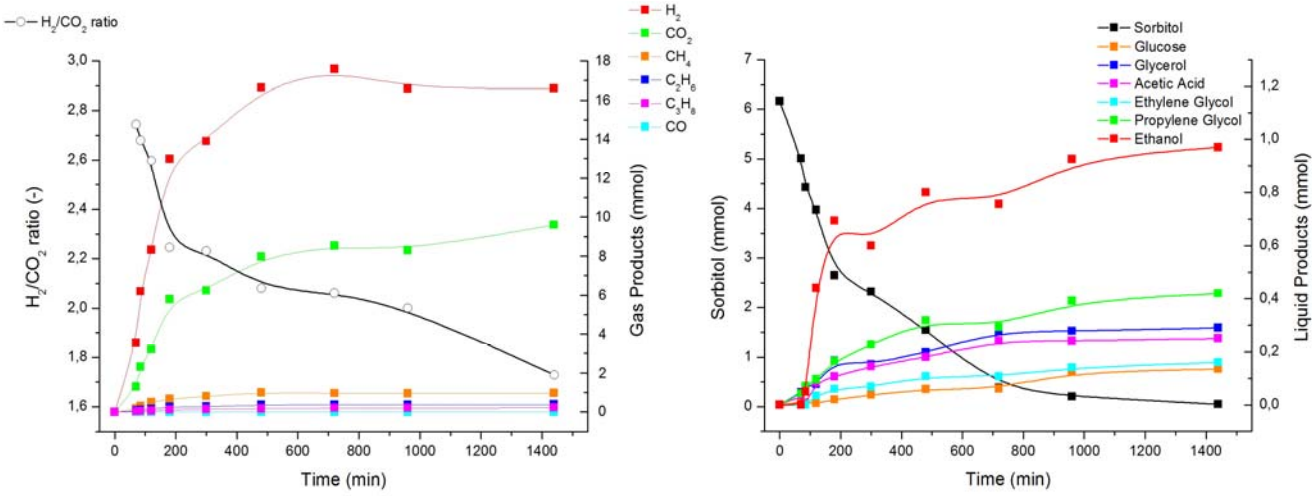

Fig. 1. Distribution of products in the APR of sorbitol. Reaction conditions: 1 wt % of sorbitol over Pt/Al_2O_3 catalyst; initial pressure = 1 bar; operative temperature = 225 °C

Figure 1 shows the results of sorbitol's conversion to gas and liquid products, which involved opposite trends of gaseous species production and H_2 selectivity. Hence, the production of H_2 increased until almost a plateau was achieved (at around 480 minutes), while sorbitol conversion progressed by preferentially forming CO_2 and alkanes. This translated into a H_2 selectivity decreasing from 84.2 % at 70 minutes to 80.7 % at 1440 minutes, and a H_2 to CO_2 ratio from 2.74 to 1.72. This behavior was attributed to the progressive APR of the liquid byproducts resulting from sorbitol conversion.

Although the trends of APR of the different substrates had similar characteristics, their reactivity was different: at a reaction time of 300 min, the conversion to gaseous products was 27.7 % for sorbitol, 37.2 % for xylose and 27.3 % for xylitol. Glucose was proven not be stable due to its degradation, which lead to the formation of a solid residue even after 120 min of reaction. In terms of selectivity, xylose had nearly half of the selectivty to H_2 showed by sorbitol and xylitol, the latter being around 82 %. Other parameters, such as the catalyst content, the pressure, sugar concentration and the temperature were also investigated, but not reported here for brevity constraints.

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OP-I-16

RECYCLING ORGANIC WASTE INTO VALUABLE FUEL

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During the last decade the volume of food production industry is steadily growing [1-2]. Disposal and recycling of organic wastes becomes a serious environmental problem for most of the processing enterprises in developing countries. Disposal of waste will improve the ecology of the environment and help us get green energy.

The technologies of high-temperature processing are based on thermal decomposition of waste without oxygen (air) at a temperature of 600-800 °C and use of microspheres air ashes as a catalyst. This is significantly speed up the process of decomposition of organic materials. In pyrolysis wastes are converted into gaseous, liquid and solid fuels.

As the object of research chosen the liquid product of pyrolysis of animal waste produced on an experimental pilot plant Complex «GR» "Research and Production Enterprise" GEOCE" [3]. An experimental industrial plant, capacity – 500 kg/h. The material balance of the pilot plant is shown in Table 1.

Table 1 – Material balance of the pilot plant for obtaining by thermolysis of animal waste [3]

Name of the product	Share in the total volume, %	Quantity, kg
Water	60	600
Organic waste materials:	40	400
absorbent coal	10	100
burning gas	12	120
hydrocarbons (oil)	18	180

The resulting liquid hydrocarbons – the synthetic liquid fuels have a density is 930,7 kg/m^3 and viscosity is 291,9 mm^2/s at 20 °C. Content of asphaltene and resin was 6 and 27,5 wt %., respectively.

The results of the elemental composition of the original the synthetic liquid fuels, selected resins and asphaltenes are shown in Table 2.

Table 2 – Elemental composition of the synthetic liquid fuels

Sample name	Content of elements, % wt.			
	C	S	H	N
Synthetic liquid fuels	73.0	0,2	9.3	4.5
Resins	69.0	0.0	7.5	4.8
Asphaltenes	72.8	0.0	7.0	9.4

Ratio of 100 H/C in the original sample of the synthetic liquid fuels was 12.7, which identify the heavy oil. It is also present in significant nitrogen content, which is not typical for oil and can be explained by a high content of nitrogen in animal tissues, and that goes into the process of pyrolysis into the core product. Ratio of 100 N/C of the resins and asphaltenes was 10.8 and 9.7, respectively. The values obtained may indirectly confirm the presence of high molecular weight hydrocarbons in the original sample of artificial liquid fuel.

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ORAL PRESENTATIONS

Section II. BIOMASS DERIVATIVES IN PETROCHEMISTRY

Catalyst application for clean syn-gas and clean hydrogen production

Lipids in petrochemical synthesis

BIOFUELS AS A PERSPECTIVE HYDROGEN SOURCE FOR FUEL CELL POWER UNITS

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Permanent fluctuations in the oil and gas prices cause the need for searching new appropriate low-cost feedstock for hydrogen production. Biofuels derived from renewable plant raw materials show high promises in this regard. They include alcohols (methanol, ethanol, butanol), oils (soybean, palm, sunflower, rapeseed, peanut), methyl esters of palm, rapeseed, and other oils (biodiesel). According to [1], the content of hydrogen in various fuels is as follows (wt. %): alcohols – 12.6-13.6, gasoline – 12-15, diesel and biodiesel – 13-16, vegetable oils – 10-12.3, fatty acid esters – 13.2-14, pyrolysis oil – 7.5. That is, the most biofuels contain ~12-13 wt. % of hydrogen.

Energy profitability of hydrogen production from the fuel is another important issue to be accounted. It refers to energy return on energy invested. If this factor is ≤ 1, the technology is economically inefficient. As shown in [2], this factor is 1-3 for biodiesel fuel, and 0.8-1.6 for ethanol. That is, the production of hydrogen from biofuels falls to the energy profitability edge. In view of this fact, strict energy efficiency requirements should be imposed on the technologies for hydrogen production for feeding fuel-cell-based power units.

The present work considers the problems related to the development of catalysts for liquid hydrocarbon fuel reforming to synthesis gas, the processes of steam and autothermal reforming of fuel to synthesis gas, membrane hydrogen separation. Mathematic modeling and calculation of a 5 kW power unit fed by hydrogen generated from biodiesel fuel will be performed.

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FLAME PYROLYSIS PREPARED CATALYSTS FOR THE STEAM REFORMING OF ETHANOL

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Introduction

Among the methods to produce H_2, Steam Reforming (SR) is one of the most common and feasible to use [1-7]. One challenge for SR at high temperature is catalyst deactivation by sintering, so that high thermal resistance is a pressing need. By contrast, it is envisaged to operate at lower temperature, to lower the heat input to the reactor. Nevertheless, catalyst deactivation may be impressive by coking, due to the formation of carbon filaments and occurs mainly over big nickel particles [8]. Additional coking may occur over acidic sites of the support. Therefore, an appropriate catalyst formulation should be found, which allows to reach the highest catalytic performance at low operating temperature (i.e. ca. 500 °C) together with proper resistance.

The aim of this work is the synthesis of catalysts for the SR of ethanol. A set of catalysts was synthesized by Flame Spray Pyrolysis (FP) and another set was prepared by impregnation of the active phase on the FP-prepared support. This high temperature synthesis was here adopted to impart suitable thermal resistance to the samples and to provide a high metal support interaction, which showed a pivotal importance to improve resistance towards coking.

Experimental/methodology

A first set of samples was directly prepared by FP, inserting in one-step the Ni-based active phase into the selected support, TiO_2 and La_2O_3 with different metal loading of 5, 10 and 15 wt %. For comparison, the same formulations have been prepared by impregnation of Ni on the FP prepared supports. The catalysts were reduced for 1h at 800 °C in a 20 vol % H_2 / N_2 gas mixture.

The samples characterization was carried out by conventional methods of XRD, BET, SEM, EDX, TEM and TPR.

Finally the activity test of the samples were performed by means of a micro pilot plant constituted by an Incoloy 800 continuous down flow reactor heated by an electric oven. Catalyst activation was accomplished by feeding 50 cm^3/min of a 20 vol % H_2/N_2 gas mixture, while heating by 10 °C/min up to 800 °C, then kept for 1 hour. For activity testing 0.017 cm^3/min of a 3:1 (mol/mol) $H_2O:CH_3CH_2OH$ liquid mixture were feed to the reactor by means of a HPLC pump (Waters, mod. 501). The activity tests were carried out at atmospheric pressure, GHSV = 2.500 h^{-1} (referred to the ethanol + water gaseous mixture) at 500, 625 and 750 °C. The analysis of the out-flowing gas was carried out by a gas chromatograph (Agilent, mod. 7980) ca. 8 h.

Results and discussion

Nickel-based catalysts at three different loadings (5, 10 and 15 wt %), supported over lanthana and titania were synthesized and tested for ethanol steam reforming at 500 and 750 °C. All of them were more active and stable at the latter temperature while at the former the impregnated catalysts with low Ni loading exhibited low H_2 productivity, mainly due to unreformed CH_4. By contrast, the FP ones demonstrated superior catalytic activity and satisfactory stability, especially with lanthana support, which effectively reduced deactivation by coking at the lowest operating temperature.

The catalytic activity has been correlated to metal dispersion and to the metal-support interaction strength. Both parameters affected also catalyst resistance to coking at 500 °C. Overall, lanthana demonstrated and interesting support due to its basic character, which prevented significant coke formation related to the acidic properties of the support. Furthermore, high metal dispersion and proper stabilization on the support allowed to limit the formation of carbon nanofilaments as deactivation mode.

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OP-II-3

EFFECT OF ELECTRIC FIELD ON CATALYTIC METHANE STEAM REFORMING AT LOW TEMPERATURE OVER Pd / CeO_2

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Introduction

The demand for hydrogen is increasing recently especially because hydrogen has been expected as a secondary energy source. Catalytic methane steam reforming (SR) is a common process for hydrogen production.

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad \Delta H^0 = 165\ \mathrm{kJ\ mol^{-1}}$$

This reaction requires high reaction temperatures, such as over 973 K, because of thermodynamic equilibrium limitation and stable methane structure. Lowering reaction temperature of steam reforming has a potential to recover low-grade waste heat with producing hydrogen. This is expected as an approach toward the improvenent in the efficiency of chemical-heat energy recovery. In our researches [1-2], we found that a steam reforming process in an electric field, called *Electreforming* (ER), showed high activity even at low temperature as 423 K. However, the effect of applying electric field to the catalyst bed on methane steam reforming is not clear. To elucidate the effect of electric field, kinetic investigations and *in-situ* IR measurements were conducted.

Experimental

1 wt % Pd/CeO_2 was prepared by an impregnation method as a catalyst. In all activity tests, a quartz tube was used for a fixed-bed flow-type reactor, as shown in Fig. 1. Two electrodes were inserted into the reactor to impose direct current (basically, 5 mA) for applying an electric field. The amount of catalyst was 80 mg, and the standard feed gas was CH_4 : H_2O : Ar : He = 12 : 24 : 12 : 72 SCCM. The preset reaction temperature was in the range from 398 to 823 K, and the product gas was analyzed by a Q-Mass. *In-situ* DRIFTS measurements were conducted at 473 K using Teflon-made IR cell and disc-shaped catalyst as a sample with applying an electric field.

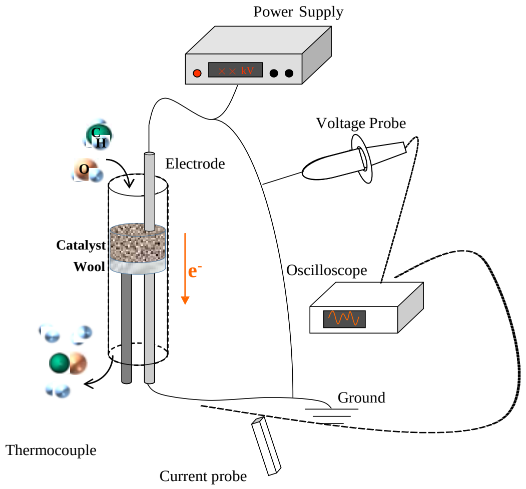

Fig. 1. Schematic image of reactor

Results and Discussions

We found that methane conversion was almost the same (around 7 %) at 473 K ER and 673 K SR, as shown in Fig. 2. At these temperatures, the dependence of raw partial pressure on the reaction rate was measured. We estimated the reaction rate equation as $r = k\ P_{CH4}{}^{\alpha}\ P_{H2O}{}^{\beta}$, and obtained $\alpha = 0.32$, $\beta = 0.79$ for ER at 473 K and $\alpha = 0.23$, $\beta = 0.25$ for SR at 673 K. The dependence of water pressure drastically increased when applying the electric field. Also, as shown in Fig. 3, the apparent activation energy decreased when applying electric field. In addition, the slope of Arrhenius plot changed around 623 K for ER. Focusing on the phenomena at low reaction temperatures, we conducted *in-situ* DRIFTS measurements. The obtained *in-situ* IR spectra are shown in Fig. 4. When applying the electric field, the amount of adsorbed methane species was drastically increased. Also, the adsorbed methane remained on the surface of catalyst to some extent even after electric field imposing. From these results, one of the effect of electric field was considered to promote the methane dissociative adsorption steps irreversibly. We also observed the activated OH species whose O-H bond was weakened about 25 kJ mol^{-1} by wavenumber shift. It is supposed that this activated water species on the surface of the catalyst is important for *Electreforming* and enhances total reaction rate.

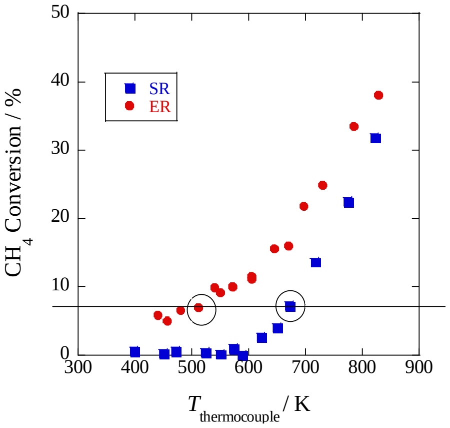

Fig. 2. Activities for SR and ER over 1 wt % Pd/CeO$_2$

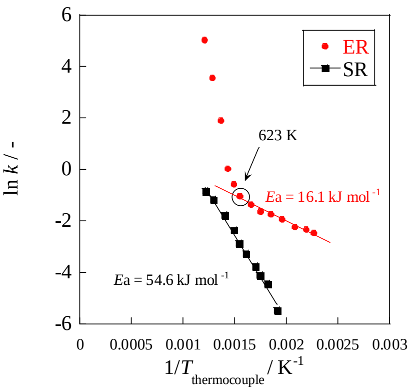

Fig. 3. Arrhenius plots

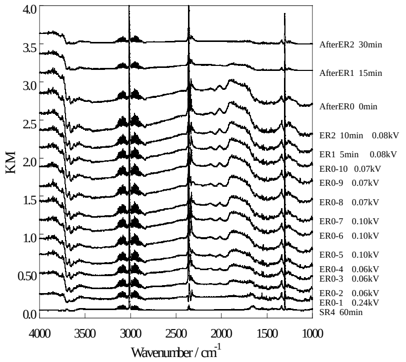

Fig. 4. *In-situ* IR spectra

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DRY AND STEAM REFORMING OF FERMENTATION PRODUCTS INTO SYNGAS OVER POROUS CERAMIC Ni(Al)-Co-CONTAINING CONVERTERS

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Regularities of dry and steam reforming processes of fermentation products over the porous ceramic Ni(Al)-Co-containing converters prepared by self-propagating high temperature synthesis were studied.

The non-additive effect of increasing the catalytic activity of the Ni(Al)-Co_3O_4 (45(5)-50 %) converter was discovered. Specific productivity of the sample on syngas exceeds that for other compositions by more than two times and reaches 150000 l/h·dm^3 (for dry reforming of ethanol). It was stated that the activity on syngas and the selectivity on hydrogen over the converter are higher than those of granular catalyst of the same composition. It was established that modification of the porous ceramic converters by Ce-containing components enhances their activity in ~ 1.5 times. The sequence of the reactions in the dry reforming of methane process over the Ni(Al)-Co granules was studied by thermogravimetry (TG). Structure of converter materials was studied by BET, XRD, SEM, TEM, EDX, XAFS methods. The role of the Al addition to Ni-Co precursors and its influence to activity in the conversion of fermentation processes was investigated.

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HYDROGEN PRODUCTION BY CATALYTIC REFORMING OF RENEWABLES FOR POWER GENERATION IN SOFC

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The carbon-based fuels have created serious environmental problems of climate change due to the emission of huge amounts of greenhouse gas, which has exceeded the capacity that can be absorbed by natural processes. In order to have a CO_2 neutral energy production, renewable energy sources will be one of the solutions to cut-off emissions and to gain energy security. Solid Oxide Fuel cells (SOFC) have attracted a lot of attention as one of the alternative sources of clean energy [1]. SOFC have been investigated as devices for the direct conversion of the chemical energy of a fuel into electrical, with high efficiency. The main advantage of SOFC technology is its high flexibility regarding the fuel. Due to the high operating temperature of 700-1000 °C, the SOFC is able to convert fuels directly by internal reforming and promotes rapid kinetics for energy conversion. Thus, high thermal and electrical efficiency is obtained. Our study is geared towards optimizing the processes taking place at the internal reformer of SOFC.

Bioethanol and acetic acid were considered to be attractive sustainable fuels for SOFC, both are produced based on biomass sources. Bioethanol is the most produced biofuel worldwide, likewise acetic acid is one of the most important components of bio oil. Different strategies have been proposed to produce hydrogen from ethanol and acetic acid: steam reforming (SR), partial oxidation (POx) and oxidative steam reforming processes (OSR). Using bioethanol, partial oxidation was chosen as the most effective process for its conversion in SOFC with fast start-up and response times determined by the exothermic nature of the oxidation reaction [2]. Additionally, partial oxidation reaction requires lower energy for fuel evaporation because no water is needed. All these features make partial oxidation reaction desirable for mobile application, where a compact system is needed. Using acetic acid as the fuel, steam reforming reaction is the most effective process for hydrogen production, which provides high selectivity and low coke formation [3].

Hydrogen production by partial oxidation and steam reforming are performed by similar, but complex reaction pathway, including dehydration, dehydrogenation, reforming and oxidation reactions, but also the waster-gas shift reaction. The obtained products depend on the selected reaction conditions and the choice of catalyst. Low cost metals as nickel and cobalt were used as catalysts supported on inexpensive, thermally stable metal oxides such as aluminum or zinc oxides as well as binary mixed oxides ($AlZnO_x$). The performance of the Co- or Ni-based catalysts in the partial oxidation of bioethanol and the steam reforming of acetic acid was elucidated.

The results indicate clearly that Co as well as Ni samples supported on $AlZnO_x$ mixed oxide possess higher catalytic activity in ethanol partial oxidation than the single oxide supported catalysts [2]. At 700 °C the highest hydrogen selectivity was obtained over the $Ni/AlZnO_x$ catalyst with 90 % at complete ethanol conversion followed by the $Co/AlZnO_x$ catalyst with 80 %. Over the $Ni/AlZnO_x$ catalyst selectivity to CO was 78 % and 21 % to CO_2. As byproduct only methane was formed with 0.5 % selectivity, whereas on $Co/AlZnO_x$ a higher selectivity to methane was obtained, at the expense of hydrogen production. Exactly the opposite pattern has been established in steam reforming of acetic acid. The Co as well as Ni samples supported on single oxide supports possess higher catalytic activity in steam reforming reaction than the mixed oxide supported catalysts. At 800 °C the highest hydrogen selectivity was obtained over Ni/Al_2O_3 with 56 % at complete acetic acid conversion. Selectivity to CO and CO_2 were 73 % and 27 %, respectively.

The experimental research was accompanied by a thermodynamic study. The results show that by both reactions, partial oxidation of ethanol and steam reforming of acetic acid, an hydrogen and CO rich gas is obtained which can be applied for energy generation in solid oxide fuel cells. Low price and thermally stable catalysts based on Ni or Co metals enables the reactions in the operation temperature range of SOFC with high hydrogen yield.

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EFFECT OF DIFFERENT OXIDES SUPPORT ON Ni-BASED CATALYSTS TO THE SYNGAS PRODUCTION FOR CARBON DIOXIDE (CO_2) DRY REFORMING OF GLYCEROL

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The increasing demands of biodiesel as an alternative for fossil-based energy consumption contribute to a dramatic growth in glycerol production. Therefore, the production of synthesis gas (syngas) and hydrogen is one of the promising way to benefit oversupply of glycerol production. The most common method of producing hydrogen and syngas is through steam reforming. However, steam reforming requires high-energy consumption in order to provide optimum condition for reaction to occur and promotes formation of carbon which negatively affect the stability of the catalyst due to high operation temperature. On the other hand, the glycerol dry reforming process is an attractive process as it converts carbon dioxide, a greenhouse gas into a synthesis gas and simultaneously removed from the carbon biosphere cycle. Dry reforming of glycerol is a reaction in which as the temperature increases, the favourable product formed will also be higher. Thermodynamic analysis of glycerol dry reforming performed by Wang et al. [1] suggested that carbon dioxide as the reactant will also take place in the reaction to be converted into carbon monoxide as favoured or removed from carbon biosphere cycle. Carbon dioxide conversion is higher with high temperature and atmospheric pressure is preferred and considered to be the best reaction condition in term of pressure with respect to hydrogen and synthesis gas production. The objective of this research work is to synthesize, characterize and conduct the catalytic activity test of glycerol dry reforming using nickel (Ni) at different composition as active phase supported on different oxides i.e. aluminium oxide(Al_2O_3), silicon oxide (SiO_2) and lanthanum oxide (La_2O_3) catalysts. The catalysts were prepared through wet impregnation method, in which different calcined oxides (i.e. Al_2O_3, SiO_2 and La_2O_3) were impregnated in aqueous Ni solution before underwent the calcination at 500 °C for five hours. The catalysts were characterized via X-ray diffraction (XRD), Scanning electron microscopy (SEM), Bruanauer-Emmett-Teller (BET) surface area and Fourier-Transform Infrared Spectroscopy (FTIR). The catalytic activities were tested using a fixed bed reactor at 700 °C, 1 atm with the CO_2: glycerol ratio of 1:1. It was found that 15 wt % Ni catalysts results in higher glycerol conversion and hydrogen yield for each type of oxides. This is due to the higher level of active sites in the catalyst to break the C-C bonds and contributes to higher catalytic activity compared to 5 wt % and 10 wt % Ni loadings [2]. Figure 1 illustrates the conversion of glycerol for the three catalysts at 15 wt % Ni composition. 15 wt % Ni/Al_2O_3 and 15 wt % Ni/SiO_2 shows almost similar value of glycerol conversion. The 15 wt % Ni/La_2O_3 gives a distinctive value of glycerol conversion and hydrogen yield. The result is in agreement with characterization study which indicates the higher surface area and smaller crystallites size owned by 15 wt % Ni/La_2O_3. Lanthanide species acts as structural promoter in the catalyst which finely disperses Ni particles, thus reduce the crystallites size and resulting in higher catalytic activity [3].

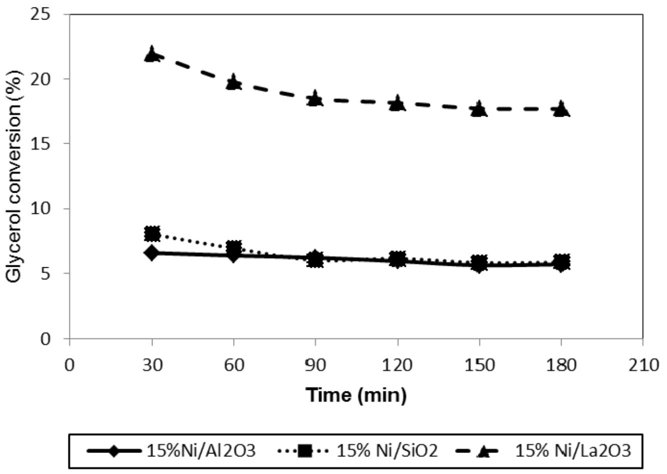

Figure 1: Conversion of glycerol versus time (min)

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HYDROTHERMAL LIQUEFACTION OF MICROALGAE IN THE PRESENCE OF HOMOGENEOUS AND HETEROGENEOUS CATALYSTS

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The continuous raise in the prices of fossil fuels and the awareness of the society challenges related to their use has recently driven a strong growth of interest on the investigation of different biochemical or thermochemical processes for the production of liquid biofuels .

In this context hydrothermal liquefaction (HTL) of terrestrial biomass seems to be promising from some process costs analyses, even if different technological hurdles are still to be overcome to reach high process efficiency [1]. For example, problems must be solved concerning the effect of biomass impurities and inhomogeneity, the necessity of using corrosion resistant materials, the technological complexity of continuous plant layout, the feeding of water-biomass mixture.

Several studies have shown that the biocrude obtained from thermochemical liquefaction of microalgae has a quite high heating value, although its oxygen and nitrogen contents are significant [2].

In this study, experiments of hydrothermal liquefaction of microalgae were carried out in near critical water in the presence of homogeneous and heterogeneous catalysts to estimate their influence on the performances of the process.

All the experiments were carried out in a 29.7 mL AISI 316 batch reactor, filled with an algal slurry at 10 wt % of biomass. The used algal biomass was constituted by Nannochloropsis gaditana dry powder. Tests were carried out at near critical conditions for water (375 °C and P > 22.1 MPa) with a reaction time of 15 minutes. Catalyst were tested both at 30 % and 60 % of reactor filling, to study the influence of the system density and pressure.

Products collected at the end of each liquefaction experiment were distributed in four different phases: a solid residue, an aqueous phase, a bio-crude oil and a gaseous mixture. The amount, the yield and the organic content of each phase were estimated. Moreover, the composition of the obtained gas was investigated by chromatographic analysis, the total organic carbon (TOC) of the aqueous phase was measured, and the biocrude oil was characterized by elemental and GM-MS analysis.

All investigated catalysts exhibited influence on the yields of the different obtained phases in terms of distribution and composition as well. Results will be shown and discussed with respect to critical product parameters, such as biocrude and gas yields, gas composition and presence of heteroatoms (N, O, S) in the obtained biocrude.

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ORAL PRESENTATIONS

Section III. CATALYTIC PROCESSES FOR BIOFUELS PRODUCTION

Catalytic interesterification and hydrocracking of lipids to kerosene and diesel fractions

Catalytic approaches for the processing of pyrolysis biomass products

STABILITY PROBLEMS OF Ni-BASED CATALYSTS IN PYROLYSIS OIL HYDROTREATMENT

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The bio-oil, which is a product of flash pyrolysis of grinded wood, is another perspective feedstock for the petrol production. However bio-oil cannot substitute traditional gasoline and diesel in the internal-combustion engines on its own owing to their lower operational properties. The main reason is the high oxygen content in above mentioned bio-fuels. The main goal of the hydrotreatment of bio-oil is to reduce the content of oxygen that is responsible for such negative properties of bio-oil as high viscosity, non-volatility, aggressivity, immiscibility with mineral oil, instability, and tendency to polymerization.

In general, the most promising approach in the hydrotreatment of bio-oil is a two-stage hydrotreatment at high pressures of hydrogen (5-10 MPa) [1]. In this case, the first stage at 150-250 °C consists in the partial deoxygenation of bio-oil components, which increases the thermal stability of partially deoxygenated products during their further hydrotreatment at higher temperatures 300-380 °C.

It should be pointed out that one cannot use traditional hydrocracking catalysts for oil-refinery at hydrotreatment of bio-fuels because of low sulfur content in original feedstock. Thus, the objective of the investigation is to develop non-sulfided catalysts for upgraded bio-fuels production. The obtained upgraded products can be used as additives to fossil crude-oil in the standard oil-refining. Since the bio-oil is specific for the processing, the catalysts for its refining should meet some special demands, namely:

- sufficiently high activity in the removal of oxygen from a wide range of organic compounds with different reactivities;
- resistance to water at elevated temperatures in an acidic medium;
- stability to coking or to the regeneration via the burning-off of carbon deposits [2-4].

These special Ni-based catalysts are referred to here as PiculaTM, characterized by a high loading of active components. The high metal loading allows improved contact of the oxygenated compounds with the active metals, minimizing the contact area between the inactive (and sometime acidic) support and the reactive oxygenates, to suppress undesirable re-polymerisation reactions. For these Picula family SiO_2 is generally used as stabilizer and the support is characterized such that highly dispersed nickel particles are uniformly distributed throughout the particle volume. Some catalysts of that type were already examined in hydrotreatment of model compound of pyrolysis liquids and indeed were shown to be very promising. Long time on stream production of fully deoxygenated pyrolysis liquids has been carried out with Picula catalyst. It was showed that the Pocula catalyst (Ni-Cu-SiO_2) was deactivated because of leaching, coking and agglomeration. As was noted in [2] Mo can improve Ni-based catalysts properties. In the present study three catalysts were tested: *Picula* and two Mo-modified Picula catalysts with different Mo content, denoted as *Picula-Mo-1* and *Picula-Mo-2.*

Van Krevelen plot of upgraded oils obtained during PO stabilization over Picula family catalysts is presented on the figure 1. Upgraded oils obtained over Picula-Mo-1 catalyst have the highest H/C atomic ratio, while products obtained over non-modified Picula possess the lowest H/C, which correlates with H_2 consumption data. The results of catalysts testing in continuous mode correlate with those obtained during batch experiments. Mo-modified Picula-Mo-1 exhibited the highest hydrogenation activity, the catalyst with higher Mo loading (Picula-Mo-2) possessed somewhat lower activity, and non-modified Picula performance in HDO of pyrolysis oil was the worst. Thus, it is likely that modification by Mo allowed improving of catalysts stability under the process conditions, while non-modified Picula showed the lowest stability. In the next work fresh and spent catalysts characterization is provided to make a correlation between their properties and activity shown in HDO of PO.

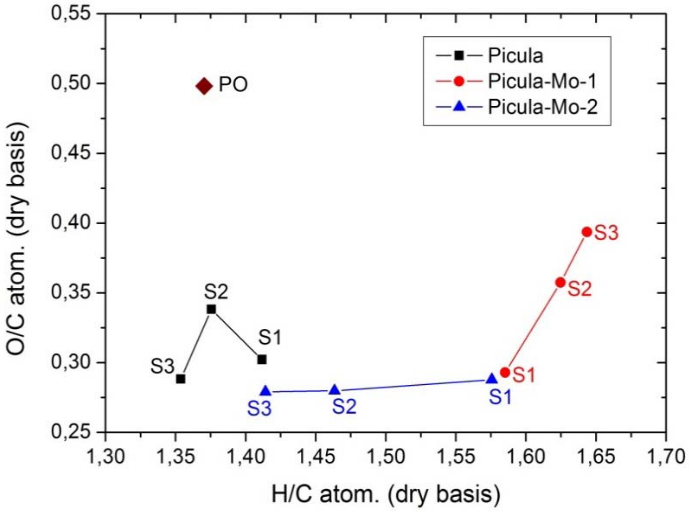

Figure 1. Van Krevelen plot of upgraded oils obtained during PO stabilization over Picula, Picula-Mo-1 and Picula-Mo-2 catalysts in continuous flow regime. For Picula catalyst: samples S1, S2 and S3 were

taken after 2nd hour, 7th hour and 10th hour of reaction, correspondingly. For Picula-Mo-1 catalyst: S1 (2nd h), S2 (7th h) and S3 (13th h). For Picula-Mo-2: S1 (2nd h), S2 (6th+7th h) and S3 (13th+14th h).

It was shown that Picula catalyst modification by Mo results in considerably higher activity demonstrated by the catalyst in target HDO process. According to the catalysts characterization by a number of physico-chemical methods, addition of Mo results in considerable improvement of catalyst stability and thus higher efficiency of HDO process. TGA and HCNS-O analysis of spent samples have shown that modified systems exhibit higher stability to coking. According to XRD study, thermal stability of these catalysts (in terms of active component agglomeration) becomes improved as well. The investigation of Picula and Picula-Mo-1(2) stability to corrosion was carried out. The kinetics of catalysts leaching was studied using 1M acetic acid water solution. Such acidic solution was chosen to model pH (around 2-3) of a real feed − pyrolysis oil. It was shown that Mo-modified Picula catalysts possess twice higher stability against leaching under the treatment conditions (based on residual mass) if compared with non-modified Picula. It is proposed that the main explanation of all those positive effects observed for Mo-modified Picula catalysts is the formation of NiCuMo solid solutions with different composition. According to the catalysts testing in stabilization of pyrolysis oil and their stability investigation, the most promising catalyst among concerned was Picula-Mo-1 with 18 wt% of Mo in its composition.

Acknowledgements

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CHARACTERIZATION STUDIES OF WASTE BIO-DERIVED FEEDSTOCK

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Lately research efforts are focused on the valorization of waste bio-feedstocks towards the selective production (via refining processes like hydroconversion, catalytic cracking etc.) of specific cuts of higher value, such as diesel and jet fuels. Thus, hydrocracking and especially hydroisomerization of long chain paraffins over novel, bifunctional catalysts are receiving increasing attention [1]. Moreover, hydrodeoxygenation (HDO) concepts are known promising approaches for waste oils' (such as bio-oil) upgrading. The WAVES project aims on exploring new and emerging technologies in heterogeneous catalysis towards the production of aviation and road transportation fuels (i.e., gasoline, kerosene, diesel) via hydroprocessing (hydro-isomerization, hydrocracking or hydrodeoxygenation) of waste and/or renewable bio-feedstocks (vegetable oil, F-T waxes, algae oil and bio-oil) via the development of new and selective catalysts with tuneable properties. Various waste feedstocks, such as high acidity vegetable oil, algae oil, F-T waxes and biomass pyrolysis oil from 5 different biomass feedstocks, have been collected for this purpose.

The current work presents the qualitative and quantitative analysis of bio-oils originating from different biomasses by GCxGC-ToFMS. A calibration method using an internal standard has been developed and employed for the analysis of bio-oils produced after the pyrolysis of different biomass samples [2,3,4]. The analysis revealed the important effect of the feedstock on the quality of the bio-oil. In particular the pinewood bio-oil is rich in phenolic and carbonyl compounds (Figure 1), while the rapeseed bio-oil is very rich in long chain organic acids and presents high peak density in the hydrocarbons area (Figure 2). On the contrary, the pyrolysis of manure results in distinctively different bio-oils, with a readily separated aqueous phase, rich in low molecular weight organic acids, hydroxyacetone and levoglucosan.

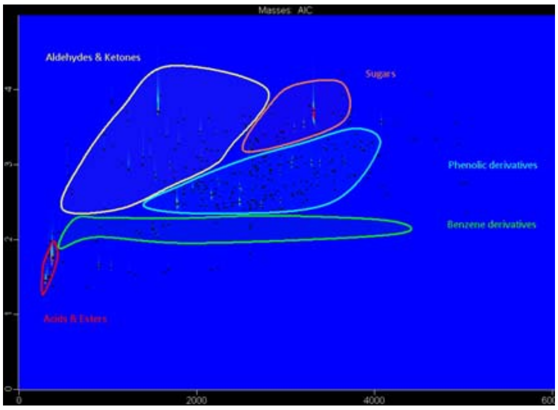

Figure 1: GCxGC-ToFMS chromatogram of pinewood derived bio-oil

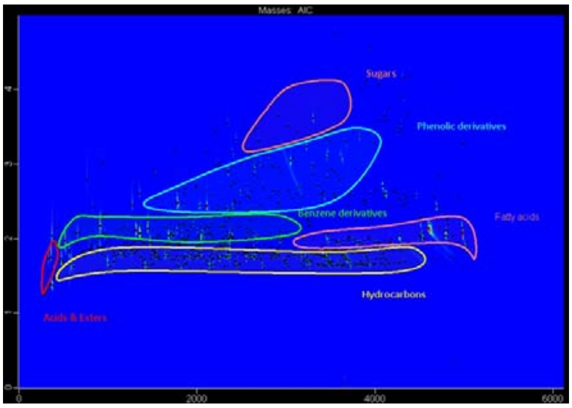

Figure 2: GCxGC-ToFMS chromatogram of rapeseed derived bio-oil

The presented work highlights the ability of the GCxGC-ToFMS technique to qualitatively and quantitatively characterize the bio-oils, both the aqueous phase and the organic fraction, in view of elucidating how each feedstock's varying properties matches the different needs for quality improvement – upgrading towards fuel production.

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OP-III-3

KETONISATION OF CARBOXYLIC ACIDS OVER METAL OXIDE AND ZEOLITE CATALYSTS IN THE GAS PHASE

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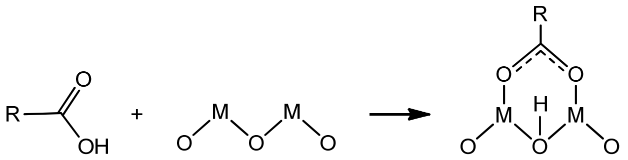
Carboxylic acids, readily available from natural resources, are attractive as renewable raw materials for the production of value-added chemicals and bio-fuels [1]. Ketonisation of carboxylic acids, $2\ RCOOH \rightarrow R_2CO + CO_2 + H_2O$, is employed as a clean method for the synthesis of ketones and upgrading biomass-derived oxygenates, e.g., bio-oil obtained from fast pyrolysis of biomass. Much current research is focussed on ketonisation of carboxylic acids using heterogeneous catalysis [2].

Here we report that Zn^{II}-Cr^{III} mixed oxides are active and durable catalysts for ketonisation of carboxylic acids (acetic and propionic) in the gas phase to yield acetone and 3-pentanone, respectively. We also report on silicalite-1 as an environmentally benign non-metal ketonisation catalyst. Insights into reaction mechanisms are also provided.

Bulk Zn-Cr mixed oxides with a Zn/Cr atomic ratio of 1:1–20:1 were found to be active catalysts for the gas-phase ketonisation of acetic and propionic acids to form acetone and 3-pentanone, respectively, at 300–400 °C and ambient pressure [3]. Zn-Cr (10:1) oxide showed the best performance, significantly exceeding that of the parent oxides ZnO and Cr_2O_3. The catalytic activity was further enhanced by supporting Zn-Cr (10:1) oxide on TiO_2 and Al_2O_3. With 20 % Zn-Cr(10:1)/Al_2O_3, ketonisation of propionic acid occurred with 97 % selectivity to 3-pentanone at 99 % conversion at 380 °C and stable activity for at least 24 h on stream (Fig. 1). By its performance, Zn-Cr (10:1) oxide is on a par with the best ketonisation catalysts reported so far, e.g., CeO_2-Mn_2O_3.



(1)

The FTIR spectrum of acetic acid adsorbed on Zn-Cr (10:1) (Fig. 2) is similar to those reported previously for other metal oxides and indicates the bridging mode for acetate bonding (eq. 1) [3]. It is conceivable that over Zn-Cr oxides ketonisation occurs via the β-ketoacid intermediate route, which is considered to be favourable for amphoteric oxides [2].

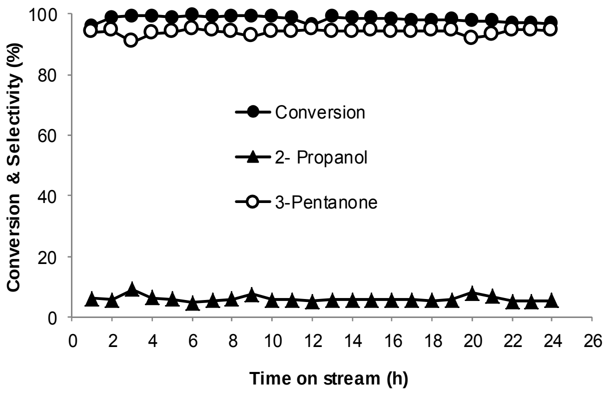


Fig. 1. Propionic acid conversion and product selectivity over 20 % Zn-Cr(10:1)/Al_2O_3 vs. time on stream (0.2 g catalyst, 380 °C, 1 bar pressure, 20 mL/min N_2 flow rate, 2 vol % propionic acid) [3]

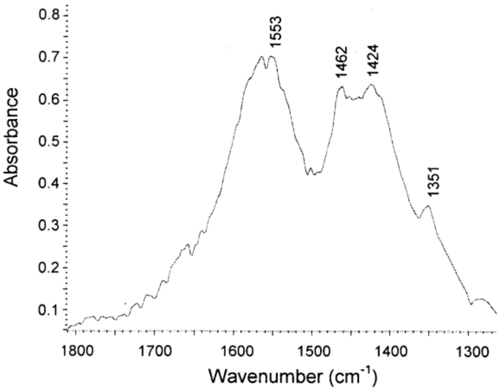


Fig. 2. FTIR spectrum of acetic acid adsorbed on Zn-Cr (10:1) oxide after evacuation at 160 °C/10^{-5} bar/1 h [3]

Amorphous silica and crystalline silicalite-1 (MFI structure) are demonstrated to be active and environmentally benign non-metal catalysts for propionic acid ketonisation at 450-500 °C [4]. Silicalite-1 was particularly efficient, and its ketonisation selectivity increased by a base modification probably through generation of silanol nests, which may be the active sites in the base-treated silicalite-1. Evidence for silanol nest formation was obtained by FTIR spectroscopy. The silicalite catalyst showed a stable performance at 500 °C for at least 28 h with 84-92 % 3-pentanone selectivity at 93-80 % propionic acid conversion.

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ETHANOL ORGANOSOLV LIGNIN DEPOLYMERISATION WITH HYDROGEN OVER NOBLE METAL CATALYSTS

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In the bio-based economy lignin is the only resource for aromatic chemicals and fuels, and catalysis is regarded to be the key technology for its valorisation [1]. In addition, depolymerisation by hydrogenolysis is considered to be the most promising method to produce phenols from lignin [2]. In this work, lignin depolymerisation was studied with hydrogen and the following catalysts: commercial 3 wt-% Pd/C as well as 1 and 3 wt-% Pd/ZrO_2 prepared by ourselves (Table 1).

Experiments were carried out using a 100 ml batch reactor equipped with a spinning basket stirrer. In a typical experiment 1 g ethanol organosolv lignin (EOL, beech, Fraunhofer) was heated to 300-400 °C in ethanol with the catalyst. The reactor was pressurised with 10-50 bar hydrogen before heating. The analysis methods were GPC, elemental analysis, GC/MS and pyrolysis-GC/MS. The catalysts were characterised with physisorption, H_2 chemisorption, XRF and ICP-AES.

The products were divided into volatiles/gases, ethanol solubles, THF solubles (ethanol insolubles) and char. Gases were not analysed and volatiles were evaporated with the solvent ethanol in the preparation of the GC/MS sample. The amount of monoaromatic compounds and dimers (light compounds) was estimated from the GC/MS analysis of the ethanol solubles. The rest of the ethanol solubles are named heavier compounds. Furthermore, the most significant monomers were quantified by GC/MS.

In the mildest conditions, 300 °C and 10 bar, lot of char was formed (15-20 % of lignin). The most remarkable difference was that much more volatile/gaseous compounds were formed with the catalysts, particularly with the Pd/C catalyst (32 % of lignin), than without a catalyst.

Table 1. Catalyst characterisation results

Catalyst	Surface Area (m^2/g)	Metal Amount ICP-AES (wt%)	Metal Dispersion (%)
3 wt-%Pd/C	na	2.15	na
Calcined ZrO_2	77.2		
1 wt-% Pd/ZrO_2	73.8	0.42	27.0 (1[a])- 54.0 (2[a])
3 wt-% Pd/ZrO_2	73.1	2.18	9.31 (1[a])- 18.62 (2[a])

[a] H_2 adsorption stoichiometry

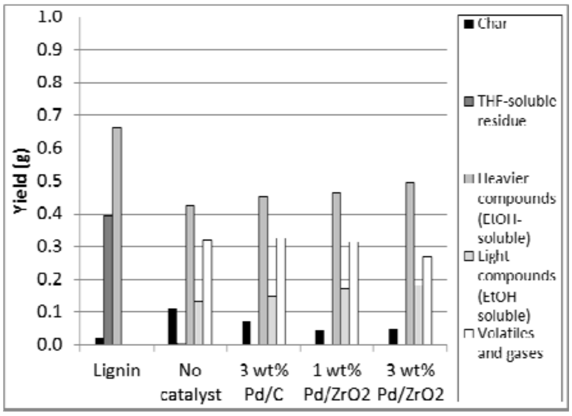

Figure 1. Lignin hydrogenolysis yields at 400 °C and 50 bar

In more severe conditions (50 bar), less repolymerisation took place. The 3 wt-% Pd/ZrO_2 catalyst was the best in preventing the char formation. Char was almost completely avoided with the 3 wt-% Pd/ZrO_2 catalyst at 300 °C and 50 bar. In the most severe conditions, 400 °C and 50 bar (Figure 1), the amount of light compounds (15-18 % of lignin) was the highest. In addition, the amount of volatiles/gases was high; 27-32 % of lignin.

As a conclusion, the hydrotreatment of the EOL on the noble metal catalysts has a high potential. However, more extensive catalyst screening and process concept development is required.

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OP-III-5

EFFECTS OF PROMOTION TECHNIQUES ON ZSM-5 ACTIVITY IN CONVERSION OF ALCOHOLS TO FUEL RANGE HYDROCARBONS

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Introduction

Fermentation broth obtainable from organic materials is a potential source of ethanol [1]. The vision of using ethanol from fermentation as a universal feedstock for production of chemicals and fuels is surely one of the promising routes towards sustainable production. Bioethanol could be dehydrated to yield ethylene which could undergo a number of reactions that will produce priceless chemicals. The product distribution of ethanol conversion is majorly determined by the quality of ethanol, operating conditions as well as the catalyst employed in the process. While zeolites have been known to show good activity in ethanol conversion to fuel range hydrocarbons, other catalysts like cerium oxide are known to favour the production of hydrogen. The Fischer-Tropsch process uses iron and cobalt catalysts for the production of different hydrocarbons [2]. The activity of these active components could also play a vital role in the transformation of ethanol to fuels and petrochemicals. This work investigates different techniques of promoting synthesized ZSM-5 zeolites with iron, cobalt and nickel as well as the efficiency of techniques with respect to catalyst activity and selectivity.

Experimental/methodology

A series of ZSM-5 catalysts were synthesized hydrothermally using aluminum salts and water glass as sources of alumina and silica respectively. The reagent composition was determined by the target ZSM-5 SiO_2/Al_2O_3. The pH of the batch mixture was kept below 10.8. The batches were further aged at different times (0-48 hrs.) and crystallization was done at different temperatures and times not exceeding 200 °C and 96 hours respectively. The produced crystals were processed by filtration, calcination and protonation to synthesize the desired protonated form of the catalyst. A commercial zsm-5 was also purchased from Zeolyst for comparative studies with the in house catalyst.

Nitrates of cobalt and iron were used for promotion at different loadings (5 %, 10 % and 15 %). Mechanical mixing, co-precipitation and incipient wetness impregnation were applied as promoting techniques to enhance catalyst performance. The synthesized catalysts were characterized using XRD, BET, XRF and SEM.

The catalyst activity was tested using a fixed bed reactor at different space velocities and temperatures in the range of 200-450 °C. The feed used include ethanol and water mixtures of various composition, isopropanol and butanol. Other alcohols were investigated so as to have a better understanding of the most probable reaction path during ethanol conversion.

Results and discussion

Powder XRD patterns of the catalyst synthesized confirmed the presence of 2 theta values for the target ZSM-5 catalysts. Figure 1 shows the diffractogram of the synthesized ZSM-5 catalyst. The presence of the ZSM-5 characteristic peaks at 2 theta = 7-9° and 23-25° further confirm the successful synthesis of ZSM-5. All the synthesized material had relative crystallinities of not less than 90 % when compared to the commercial ZSM-5 catalyst. The BET surface area and particle sizes are all seen to be a function of aging. The SEM analyses further confirmed that the zeolites formed were crystalline and had different morphologies depending on the technique used in incorporating the promoter and synthesis conditions. Figure 2 shows the micrograph of un-promoted ZSM-5 with average particle size of 0.2 μm. The incorporation of metals altered both the particle morphology as well as size.

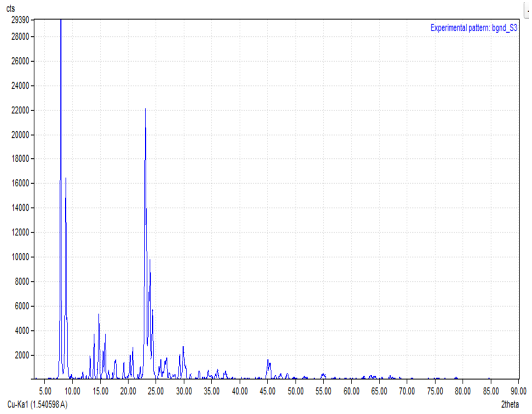

Figure 1. Diffractogram of synthesized ZSM-5

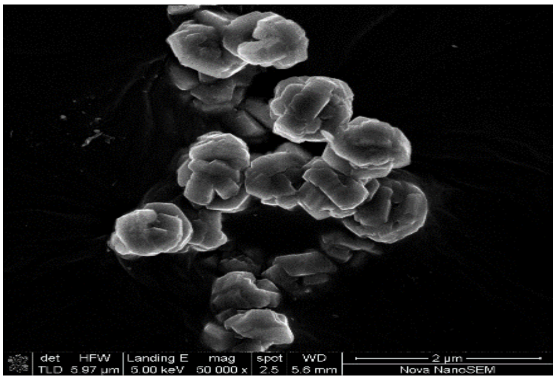

Figure 2. Micrograph of synthesized ZSM-5

All the catalysts showed 100 % activity for ethanol and isopropanol conversion with liquid hydrocarbons forming a significant amount of the products. Loading of 5 % iron oxide on the commercial catalyst by incipient wetness impregnation showed selectivity to gasoline range hydrocarbons of 72 % in the liquid products whereas the in house catalyst showed a better selectivity of 98 % during ethanol conversion. Co crystallization of both commercial and in house ZSM-5 showed different selectivity when compared to the un-promoted ZSM-5. However, 5 % loading of nickel showed the highest selectivity towards gasoline range hydrocarbons (99 %) when ethanol was used as a feedstock. Conversion of isopropanol shows that promoting the ZSM-5 with both iron had more significant changes to hydrocarbon selectivity when compared to promotion with cobalt oxide. Promoting the in house ZSM-5 with 5 % Co did resulted in a selectivity towards gasoline of 63 % which was slightly less than that obtained from the un-promoted commercial ZSM-5 promoting with Iron under the same conditions shows 78 % selectivity towards gasoline range hydrocarbons. In all three cases, the selectivity for diesel range hydrocarbons was less than 30 %.

Conclusions

ZSM-5 catalyst have been successfully synthesized and characterised, various promotion techniques and promoters used on ZSM-5 catalysts showed that both the promotion techniques as well as promoting agents had a significant impact on the product distribution. It has been observed that ethanol as well as isopropanol could serve as potential sources of hydrocarbons in the fuel range. Finally the operating parameters greatly influence the product distribution of alcohols over ZSM-5 catalysts.

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BIOREFINERY PROCESSES FOR GREEN FUELS AND HYDROGEN GENERATION: CATALYTIC STUDY IN THE HDT REACTIONS OF O-XYLENE MODEL COMPOUND

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Abstract

Several CoMo and NiMo supported catalysts were prepared, sulfided and tested in the HDT reactions of o-xylene model compound. Cobalt based catalysts show a higher acidic character, which drives to a larger activity versus both isomers and polycondensated products. Then, the metal properties affects the catalytic pathway, leading to preferential formation of p-xylene on $CoMoS_2$ catalysts.

Introduction

In recent years, the quality and the preservation of environment has been at the center of all society issues, prompting the development of "ultra clean fuels" and, in turn, introducing new challenges in hydrotreating [1]. On the other hands, the development of more efficient technologies calls for the development of timely designed "energy vectors" to achieve the industrial targets in terms of thermal efficiency, performance, emission, supplying, safety and manufacturing.The total replacement of the fossil fuels with renewable energy sources is the challenge for the future. In this, bio-oil for its easily availability, CO_2 neutrality, insensitivity to market fluctuations, low sulfur and metal content, can play a key role for the future energetic system, for both stationary and mobile applications [2]. The crude bio-oil can be used directly as boiler fuel, however, it needs of further upgrading for the more demanding utilizations such as transportation fuels and hydrogen source [3,4]. One of the more valued upgrading route is the catalytic hydrotreating (HDT), employing supported CoMo or NiMo catalysts. In spite of high activity, this catalysts soffer of strong limitation due to their acidic character which promote undesired side reactions such as cracking, polymerization and isomerization, leading to catalyst deactivation by coke formation [5]. Despite intensive efforts, the role and the nature of acid sites is still unclear. Therefore, the work aims to evaluate the influence of acid character on the catalytic HDT reactions of o-xylene model compound.

Results

The catalytic properties of catalysts were proved at 250-350 °C and 10-20 atm by using a laboratory micro-plant equipped with a AISI 316L stain steel PF-reactors, connected to GC for the analysis of the composition of reactants and products. While the physical-chemical properties of samples were characterized by XRF, XRD, XPS, TG-DSC analysis and N_2 physisorption. Then, the effect of Co and Ni promotion on catalytic pathway of MoS_2/Al_2O_3 systems were valued by comparing the catalytic performance of samples in term of reaction rates, as shown in Figure 1. Namely, $CoMoS_2/Al_2O_3$ catalyst promotes majourly isomerization and polimerization reactions than direct hydrogenation, mirroring a larger acidic character.

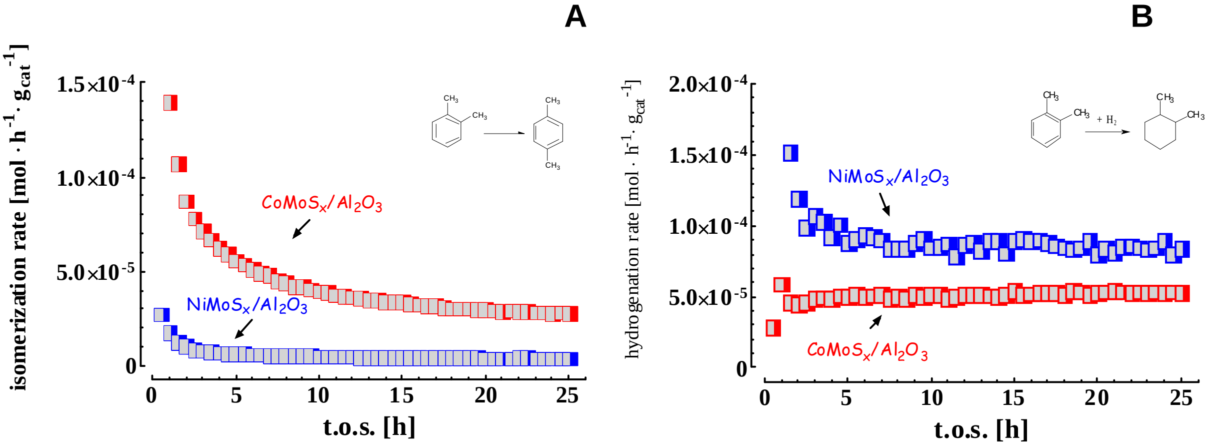

Figure 1. Isomerization (A) and Hydrohenation (B) rates of o-xylene versus time-on-stream

Conclusion

The effectiveness of HDT processes of o-xylene model compound has been assessed. The different acidic character of catalysts affects the catalytic pathway of o-xylene hydrogenation.

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Acknowledgements

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TECHNO-ECONOMIC COMPARISON OF Pt/Al_2O_3, Ni-Mo AND Co-Mo/Al_2O_3 CATALYSTS ON BIO-OIL HYDRODEOXYGENATION

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A process model was developed in Aspen Plus® for a 72 metric ton/day fast pyrolysis and bio-oil hydroprocessing plant. The impact of the hydrodeoxygenation catalysts on fuel yield and product value is investigated in this study.

Introduction

To meet the CO_2 emission reduction target in the transport sector by 2050, biofuels are projected to provide 27 % of total transport fuel mix [1]. Bio-oil derived from biomass fast pyrolysis can be upgraded into transport biofuels via hydrodeoxygenation (HDO) and hydrocracking. The HDO step reduces the oxygen content of the bio-oil, while the hydrocracking step breaks down the resultant heavy ligneous-aromatic compounds from HDO into lighter hydrocarbons. The HDO catalyst type is an important process variable that influences hydrocarbon product yields and the consequent product value (PV), which is the minimum price of the product required for a net present value of zero. The aim of this work is to investigate the impact of the HDO catalyst on the fuel yield and product value. Performance of three different catalysts, Pt/Al_2O_3, sulfided Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 is evaluated.

Materials and Methods

A rate-based process model was implemented in Aspen Plus® V8.2 [2] and validated with experimental data from literature [3; 4]. Equipment sizing and cost estimation was carried out in Aspen Process Economic Analyser® and PV was estimated from discounted cash flow analysis assuming the plant operates for 20 years at a 10 % annual discount rate. The specifications of the hydrodeoxygenation catalysts included in this study are presented in Table 1.

Table 1. Hydrodeoxygenation catalysts specifications [4]

Catalyst	Composition	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (Å)
Pt/Al_2O_3	5% Pt	100	0.52	100
Co-Mo	3% CoO, 15% MoO_3	200	0.45	94
Ni-Mo`	3.5% NiO, 15.5% MoO_3	200	0.46	88

Results and Discussion

The fuel yields and PVs obtained from HDO carried out at 400 °C, 87.2 bar and WHSV of 2 hr^{-1} over Pt/Al_2O_3, sulfided CoMo/Al_2O_3 and Ni-Mo/Al_2O_3 catalysts are depicted in Figure 1 and Figure 2 respectively.

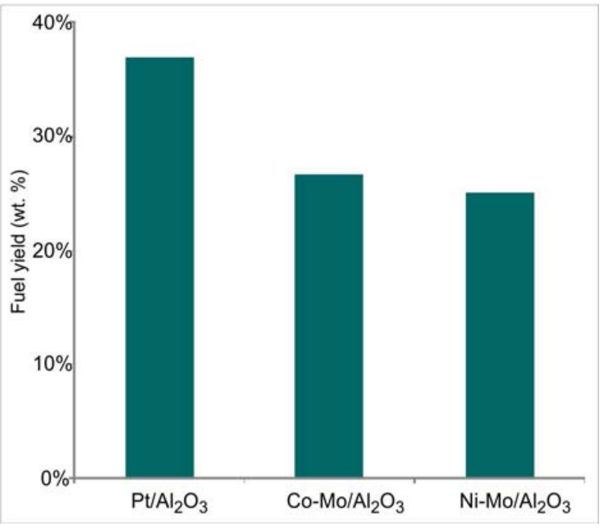

Figure 1. Fuel yield from the Pt, Co-Mo and Ni-Mo Catalysts

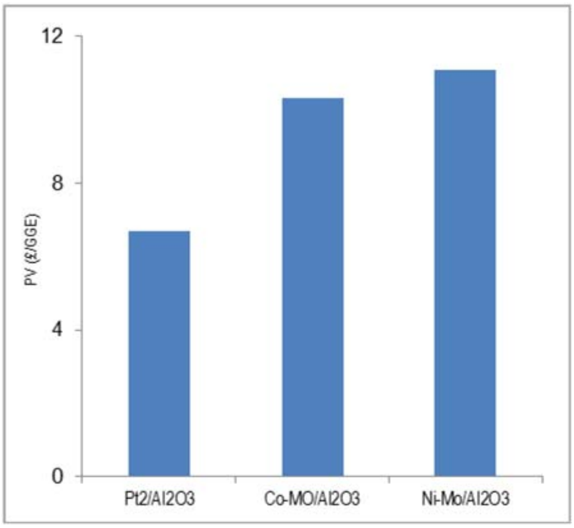

Figure 2. Effect of Hydrodeoxygenation catalysts on PV

Conclusions

In this study, simulation results showed that the hydrodeoxygenation catalyst type is a key process variable that may influence the commercial viability of the process. Pt/Al_2O_3 exhibited the highest fuel yield and lowest PV, being the most cost-effective of the three catalysts. Co-Mo and Ni-Mo catalysts gave rise to similar fuel yields, which were considerably lower than that obtained from the Pt-based catalyst. Overall Ni-Mo/Al_2O_3 is the least economical of the three catalysts.

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HYDRODEOXYGENATION OF PLANT LIPIDS FOR BIOFUELS PRODUCTION USING Ni-BASED CATALYSTS MODIFIED BY Mo

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World fuel demands are supposed to increase over the next few decades. Renewable biofuels are needed to partially displace petroleum derived transport fuels [1] and diversify local energy source in some region. Vegetable oils and biodiesel have drawbacks that lead to problems in the long-term operation of internal combustion engines [2]. Removing of oxygen from esters (biodiesel) and triglycerides by hydrodeoxygenation is required for production of hydrocarbons – biofuels competitive with conventional fossil derived fuels [3]. Ni – containing catalysts are known to be active in the hydrodeoxygenation of vegetable oils [4], Ni-Cu alloys exhibit activity in the hydrodeoxygenation of biodiesel [5], nickel-molybdenum alloys are known to have higher chemical resistance to acids as compared with monometallic nickel catalysts [6]. The aim of this study is the investigation of hydrodeoxygenation of esters in the presence of Ni-containing catalysts modified by Cu and Mo.

Hydrodeoxygenation experiments were performed in continuous flow reactor over heterogeneous catalysts. The hydrodeoxygenation catalysts performance was tested at P = 1 MPa and 300 °C. Methyl palmitate and ethyl caprate mixture was used as a substrate. LHSV was 3 h^{-1}. Catalysts fraction was from 0.2 to 0.5 mm and was reduced before reaction at 520 °C and P = 0.1 MPa by hydrogen. The gas products obtained in the hydrodeoxygenation reaction were analyzed by GC during the experiments, liquid phase was analyzed by GC and product identification was made using GC-MS technique.

In our work Ni/Al_2O_3 catalyst was modified by copper. On the one hand it was shown that increasing of copper content led to decreasing conversion of esters on the other hand the increase in the copper content led also to an decrease in the production of undesired product – methane.

Influence of molybdenum on activity of Ni-based catalyst in esters hydrodeoxygenation reaction was studied also. Ni-Cu catalyst were additionally modified by molybdenum. It was shown that yield of alkanes increased with Mo content increasing. The maximal conversion of esters has been observed over Ni-Cu-6.9Mo/Al_2O_3 catalyst (fig. 1) with alkanes as main products. According to the XRD and HRTEM data, all samples after reduction contain solid solutions with different compositions [7]. It was shown by XPS that HDO increase with increasing of 4+ oxidation state of Mo on the surface of the Ni-Cu-Mo/Al_2O_3 catalysts [7]. Kinetic model of hydrodeoxygenation reaction of ester over Ni-Cu-Mo catalyst was proposed.

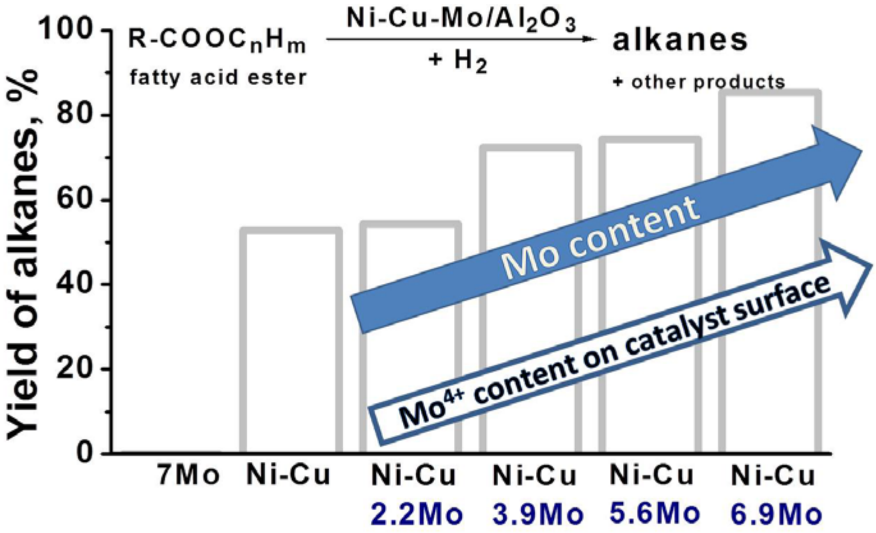

Fig. 1. Yield of alkanes in the presence of Ni-Cu-Mo/Al_2O_3 catalysts with different Mo content at 300 °C, P_{H_2} = 0.25 MPa and LHSV = 3 h^{-1}

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ENHANCED MODELING OF REACTORS WITH MINICHANNEL PACKINGS OPERATED IN GAS-LIQUID TAYLOR FLOW MODE

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Gas-liquid Taylor flow in straight mini-channels and micro-channels is used in an emerging way in process engineering and chemical reaction engineering. The specific properties of Taylor flow intensify mixing as well as heat and mass transfer and favour an application in chemical reaction processes. In particular, heat and mass transfer benefit from the large surface-to-volume ratio, short diffusion lengths and circulation vortices. Research of the last decade reports several advantages of tubular reactors with a monolithic or honeycomb packing over conventional reactors such as stirred tank reactors and randomly packed bed reactors with respect to space-time-yield and selectivity [1-2].

In order to simulate the reaction processes in reactors with minichannel packings, the mass and energy balances for the flow channel and the porous washcoat layer are combinded to form the reactor model. This model contain empirical correlations to describe reaction kinetics and mass transfer processes. The balances are solved numerically to predict concentration profiles, conversion and selectivity.

Most of the existing models are one dimensional, consider a catalyst efficiency of 100 % and neglect the energy balance. Only De Deugd et al. [3] regard the change in bubble size due to the gas consumption of the chemical reaction. The impact of this physical effect is pronounced at high reaction rates and long channels. Under these conditions, remarkably differences between channel inlet and outlet in terms of the phase velocities, the specific interfacial areas as well as mass transfer rates are expected.

This paper presents an extended pseudo-two-dimensional model for a single reaction channel with Taylor flow which is based on the models of Bauer et al. [4] and Haase et al. [5]. It considers diffusion inside the washcoat, the gas bubble size reduction and the energy balance. Based on simulations for the hydrogenation of cinnamaldehyde, aspects of mass transfer, favorable operating conditions and the channel diameter will be discussed in detail.

Exemplarily, the impact of the channel diameter and the initial gas holdup on reactor performance will be discussed in the following.

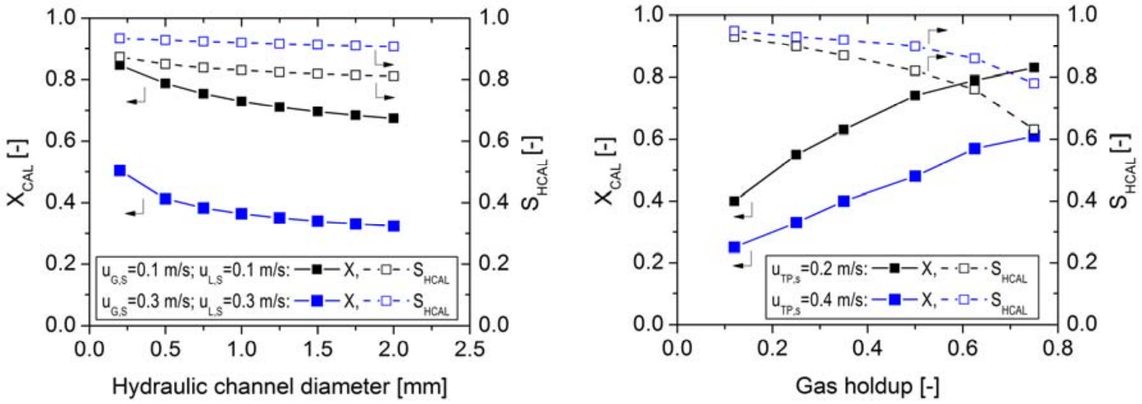

Fig. 1. Impact of channel diameter (left) and gas holdup (right) on the simulated conversion and selectivity of the process for different two-phase velocities

The simulations demonstrate that small channels and high gas holdups provoke a high conversion of cinnamaldehyde (CAL) as illustrated in Fig. 1. This is mainly caused by increased mass transfer rates for hydrogen due to smaller diffusion barriers of thinner liquid films in small channels and due to larger interfacial areas for the gas-solid transfer which is the most efficient transfer route for hydrogen. Contrary, a higher gas holdup will also provoke a lower selectivity to hydro-cinnamaldehyde (HCAL). Therefore, the presented model reperesents a virtual tool to identify favourable channel designs and operational parameters for any given chemical reaction performed in tubular reactors with minichannel packings operated in Taylor flow mode.

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COUPLING REFORMING PROCESSES WITH FISCHER-TROPSCH SINTHESYS TO PRODUCE LIQUID HYDROCARBONS FROM BIOGAS

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Biogas is an attractive renewable energy source, which could give an important contribution to drive the global energy system to a sustainable scenario [1]. Because of the main problems related to the direct use of biogas, a promising alternative consists in the production of syngas by reforming processes, i.e. Dry Reforming (DR), Steam Reforming (SR) and Oxy-Steam Reforming (OSR) [2]. Based on the composition of the syngas, it can be used for the synthesis of chemicals, with special reference to Gas-to-Liquids technologies [3].

In this study, the catalytic activity of Me/CeO_2-based structured cordierite monoliths (Me=Rh, Pt, Ni) was preliminary probed in the SR of biogas (CH_4/CO_2=1.5), varying temperature (700-900 °C) at fixed S/C (3) and weight space velocity (WSV=72,000 Nml g_{cat}^{-1} h^{-1}). Structured catalysts were lined by combining the Solution Combustion Synthesis with the Impregnation Technique [4] and characterized by XRD, XRF, SEM, TEM, TPR and CO-Chemisorption. Tab. 1 summarizes the results obtained at 900 °C, highlighting the highest performance of the Rh-CeO_2-MO system, with a methane conversion of ca. 99.8 % and negligible CH_4 content in the product mixture. Then, the addition of oxygen (O/C=0.5) was evaluated on the same system in the OSR of biogas at 900 °C in order to have a syngas composition (CO:CO_2=1:1; $H_2/(CO+CO_2)$=1.3) suitable for Fischer-Tropsch conversion (Tab. 1).

Table 1. SR and OSR of biogas: methane conversion and product composition (T=900°C, WSV=72,000 Nml g_{cat}^{-1} h^{-1}; biogas composition: CH_4/CO_2=1.5)

Process	Catalyst	X_{CH4} (%)	Product Composition (%)*				$H_2/(CO+CO_2)$	CO/CO_2
			H_2	CO	CO_2	CH_4		
SR	Pt/CeO_2-MO	97.7	63.6	22.0	14.0	0.4	1.77	1.57
SR	Ni/CeO_2-MO	92.1	61.7	22.3	16.0	1.7	1.61	1.39
SR	Rh/CeO_2-MO	99.8	63.5	22.8	13.6	0.1	1.74	1.68
OSR	Rh/CeO_2-MO	100	56.6	21.7	21.7	0.0	1.30	1.00

*Dry-basis and N_2-free

OP-III-10

The obtained syngas was fed to the Fischer-Tropsch reactor, working at 250 °C and 20 bar with FeO_x-based catalysts (WSV=1,400 Nml g_{cat}^{-1} h^{-1}) [5]. The effect of catalytic (ZnO, CuO, MnO) and structural promoters (SiO_2, Al_2O_3, CeO_2) on the activity and selectivity into higher hydrocarbons has been evaluated. All systems were characterized by means of XRD, XPS, XRF, SEM, TPR, CO-TPSR and Gas-Sorption techniques. Optimized iron-ceria based catalysts feature a catalytic performance in CO_2-rich syngas conversion superior to that of conventional ones worth of industrial exploitation application. Particularly, iron-manganese-ceria catalyst (FTC-A, FTC-B) show the best catalytic performance in term of both carbon monoxide conversion and selectivity to high hydrocarbons, resulting also in the highest values of the ASF parameter (Fig. 1).

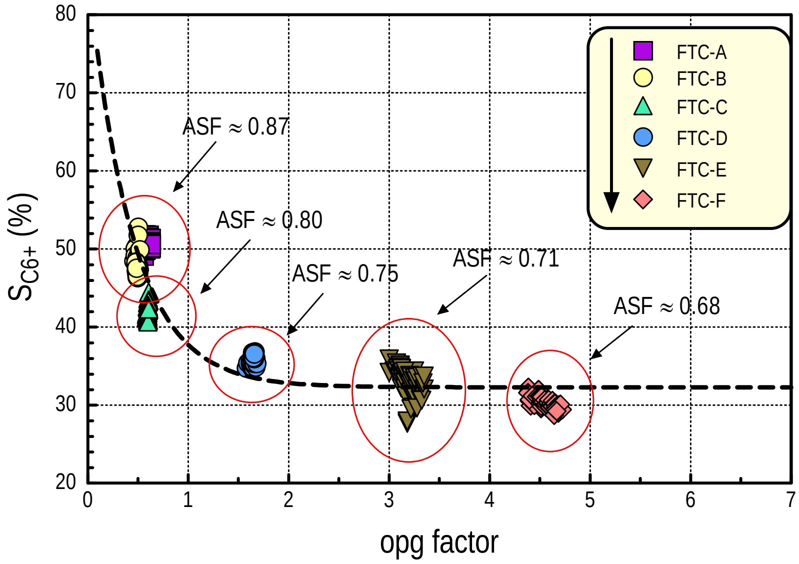

Figure 1. Fischer-Tropsch synthesis on FeOx-based catalysts: effect of catalytic and structural promoters on the selectivity to higher hydrocarbons (T=250 °C, P=20 bar; WSV=1,400 Nml g_{cat}^{-1} h^{-1}; syngas composition: $CO:CO_2$=1:1, $H_2/(CO+CO_2)$=1.3)

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METHYL PALMITATE AND 2-ETHYLPHENOL HYDRODEOXYGENATION OVER Ni_2P/SiO_2 CATALYSTS

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Transition metal phosphides are considered as the promising systems for the hydrodeoxygenation (HDO) of oxygen-containing compounds from renewables such as triglyceride-based feedstocks or biomass pyrolysis oil. Aliphatic ethers are usually chosen as the representative model components of triglyceride-based feedstock and 2-ethylphenol as the model compound of biomass pyrolysis oil.

The aim of the present work is to investigate the influence of preparation parameters on the formation of Ni_xP_y phase and on the catalytic activity of silica-supported nickel phosphide catalysts in hydrodeoxygenation of methyl palmitate (MP) and 2-ethylphenol (2-EP).

A series of silica-supported nickel phosphide catalysts were prepared by means of temperature-programmed reduction (TPR) of the nickel phosphates (A) or nickel phosphite (I) precursors, with varying Ni/P molar ratios of 2/1, 1/1 and 1/2. Two approaches were employed for the catalyst's precursor activation in a stream of H_2: *in situ* reduction in the catalytic reactor and *ex situ* reduction in the glass flow reactor followed by passivation. In the later case the catalysts should be rereduced *in situ* before the catalytic reaction at 400 °C during 2-14 hours in accordance with commonly used procedure. The catalytic properties were evaluated in trickle-bed down-flow reactor at the temperature 250-340 °C and hydrogen pressure 3.0-4.0 MPa. The reaction products were identified by GC-MS and quantified by gas chromatography system equipped with FID. The total oxygen content in the reaction mixture was determined using CHNSO elemental analyzer Vario EL Cube. The catalysts were characterized by XRD, H_2-TPR, HRTEM and XPS.

XRD and HRTEM analysis of reduced catalysts confirmed the formation of nickel phosphide phase on the surface of silica. It was shown that the Ni/P molar ratio equal to 2/1 resulted in the formation of $Ni_{12}P_5$ phase, whereas the ratio 1/1 or 1/2 produced the Ni_2P particles. Ni_2P particle with average size 4.5-6.0 nm were produced from phosphate precursor (A), while the larger particles with average size of 10.0-15.0 nm were prepared using phosphorous acid (I).

First of all the optimal conditions for reduction of Ni_2P/SiO_2 catalysts have been found by comparison of catalytic activity of samples activated *in situ* at temperatures of 550, 600, 650 °C or *ex situ* at 600 °C. It has been shown that the reduction temperature and duration both effect on MP and 2-EP conversion: the reduction of phosphate type precursors *in situ* leads to increase the catalytic activity of Ni_2P/SiO_2 catalysts in comparing with the standard *ex-situ* TPR procedure at 600 °C. MP and 2-EP differed markedly in chemical reactivity: 2-EP represented the highest resistance to conversion in deep oxygen removal process in comparison with MP and required the higher temperature to achieve a full conversion. The main products of 2-EP HDO were 2-ethylcyclohexane and 2-ethylbenzene, the appearance of 2-ethylcyclohexanone, 2-ethylcyclohexanol and 2-ethylcyclohexene as the intermidiate products pointed to the two simultaneous routes of 2-EP transformation.

The analysis of MP HDO the intermediate and final products distribution over Ni_2P/SiO_2 catalysts versus contact time let us to conclude that MP transformation to palmitic acid is the limiting stage of the reaction. Taking into account that MP can be transformed through hydrogenolysis on metal sites or by hydrolysis on acid sites the mixture of Ni_2P/SiO_2 and γ-Al_2O_3 granules were investigated in MP HDO. The noticeable synergistic effect was observed that could be explained by the higher rate of MP transformation due to acid-catalyzed reactions. The tentative reaction scheme and hypothesized mechanism of MP HDO with the participation of metal and acid catalyst's sites have been proposed.

Acknowledgements

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OP-III-12

PRODUCTION OF CLEAN BIOFUELS BY ESTERIFICATION OF FREE FATTY ACIDS USING A MEMBRANE REACTOR FOR THE CONTINUOUS WATER REMOVAL

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The process performance and economics of biodiesel production are strongly influenced by the presence in the feedstock of moisture and free acidity [1]. Usually an esterification step is necessary to eliminate the free acidity which must be reduced to levels below 1 % w/w [2-3]. Thus the improvement of the esterification step could represent one of the key points that need to be studied. Anyhow, during the esterification of free fatty acids (FFA) with alcohols (methanol, ethanol, …), water forms limiting the yield to FAME (Fatty Acid Methyl Esters) because of equilibrium restriction according to the following reaction:

$$\text{FFA} + \text{MeOH} \leftrightarrows \text{FAME} + H_2O.$$

In this study, to enhance the FAME productivity, the esterification of oleic acid with methanol was investigated using a new reaction system consisting of a batch reactor coupled with a water-permselective membrane to remove the water from the reaction medium [4-5]. Preliminarily, a systematic study was carried out without the use of the membrane by employing the A-15 resin as acid catalyst in the attempt to find the best reaction conditions for obtaining high yield to methyl ester. In such a case, FAME yields ranged from 62.5 up to 89.5 % after 15 h of reaction with a catalyst/oleic acid ratio of 5 wt/wt % and a MeOH/acid oleic molar ratio of 4 were obtained (see Table 1).

Table 1. Esterification reaction between Oleic Acid and MeOH: influence of time; influence of MeOH/Oleic Acid molar ratio and use of permselective membrane(a)

$X_{Oleic\ Acid}$	Reaction Condition		
	$R_{MeOH/Ol.ac.}$ (mol/mol)	$R_{cat/Ol.ac.}$ (wt/wt)	t (h)
62.5	2	5	2
73.0	4	5	2
73.5	8	5	2
73.0	4	5	2
83.8	4	5	5
87.3	4	5	7
89.5	4	5	15
80.1(a)	2	5	2
97.3(a)	2	5	5

By recirculating the gas phase through the permselective membrane the water was continuously and selectively removed thus shifting the equilibrium towards products and reaching an almost total oleic acid conversion (97.3 %) (see Table1). Such reactor configuration allowed to reach better results using a low alcohol to FFA molar ratio (2) in few hours of reaction (5 h against 15) with several economic and ecological advantages. Furthermore, a cleaner biofuel without water is obtained thus making possible to simplify the total process of biodiesel production.

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BIODIESEL PRODUCTION FROM MIXTURE AND INTERESTERIFICATED OILS: A COMPARISON OF THE KINETICS OF THE TRANSESTERIFICATION REACTION

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Most of the physical-chemical properties of a biodiesel are related to the fatty acid composition of the oil source.[1] However, just very few information is at our disposal in relation to the physical-chemical properties of the oil source (normally a complex mixture of triacylglyceride molecules) in which the fatty acid composition are the same, but the arrange of these fatty acid moieties on the triacylglycerides are different. The objective of this study was to carried out a comparative analysis between the kinetic of transesterification in the presence of methanol of a 1:1 mixture of soybean and castor oil and the same mixture previously interesterificated. It is important to note that the fatty acid composition for both systems is the same, but the arrange of the fatty acid moieties are different.

Interesterification

The interesterification[2,3] of the mixture was carried at 120 °C for 60 min in the presence of sodium methoxide as catalyst. Gas chromatography analysis showed that the triacylglyceride composition of the two systems are different, confirming the rearrangement of the fatty acid chains. Comparing the viscosity of the mixture and the interesterificated oils, we observed that the simple interesterificated oil is somewhat more viscous than the simple mixture of the oils (98 and 89 cSt, respectively). This result suggests that no significant difference on the kinetics of the transesterification for each oily raw material will be detected.

Transesterifications

For both source of oils, the reactions were carried out under the same reaction conditions, and the kinetic of both reactions were compared via the amount of biodiesel produced after 5.0, 10, 15, 30, 45, 60, 120, and 180 minutes. Results show that the kinetic of the transesterification of interesterified oil is slower to that of the simple mixture. This result shows that just the information of the fatty acid composition of the oil employed as the raw material for biodiesel production is not the main parameter to be considered to forecast the kinetic of the transesterification reaction.

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CASTOR OIL UPGRADING VIA THE CATALYTIC CRACKING PROCESS

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Castor bean (*Ricinus communis*) is an important oil-seed crop with unique oil. A study including 4 castor bean hybrids and 1 variety (labeled 105N), all bred for mechanized harvesting and high yield was conducted to compare these oil-seed crops in terms of oil yield and characteristics. Seed oil content is typically a quantitative trait in nature under polygenic control, influenced by the genotype, developmental stage and environmental conditions. We characterized the expression profiles of genes encoding enzymes involved in different steps of hydroxylated Triacylglycerol (TAG) biosynthesis during seed development. The specificities of these enzymes for fatty acids with different lengths and degrees of unsaturation play an important role in determining the final hydroxylated TAG composition of castor oil. Specifically, we characterized the expression profiles of glycerol-3-phosphate acyltransferase (G3PAT), lysophosphatidic acid acyltransferase (LPAAT), diacylglycerol acyltransferase (DGAT) and phospholipid:diacylglycerol acyltransferase (PDAT) in different castor bean hybrids. The expression pattern analyses demonstrated differences in gene expression among the castor bean hybrids that may reflect differences in castor oil composition.

The five castor-oils were further characterizing (Table 1) in CPERI (elemental analysis, gross calorific value, composition, acidity, density and moisture, ash content, thermal stability etc.) An in-depth characterization of the 'major components' in these vegetable oils, was also performed in CPERI with the advanced analytical technique: 2D gas chromatography (GC×GC), a most powerful separation technique to date. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was also used to determine metals and salts, as both of them could be detrimental for the catalysts used during castor-oil upgrading.

Fluid Catalytic Cracking (FCC) experiments were realized in CPERI aiming to co-process castor oil (2, 5 and 10 wt. %) with conventional VGO feedstock. Initial experiments were performed with VGO in a bench-scale catalytic cracking unit, in order to explore the optimum cracking conditions and the most efficient catalyst, chosen between several commercial catalytic materials. The Short Contact Time – Microactivity Test Unit, (SCT-MAT) available in CPERI/CERTH is fully automated, equipped with a fixed-bed plug-flow reactor [1]. Experiments were realized at different conversion levels, varying the catalyst to oil (C/O) ratio. Variation of C/O is achieved by retaining the delivered feed (pure VGO or VGO/castor-oil mixtures) to the reactor constant (1,5 g) and changing the mass of catalyst. The reaction temperature was 560 °C and the reaction time (time of feed injection) was 12 s. A N_2 flow of 30 cm^3/min was then (after the 12 s of injection) applied in order to purge the catalyst bed and remove any sorbed hydrocarbons. The reactor outlet stream was passed though a glass receiver cooled at 0 °C in order to condense the liquid products, while the non-condensable gases were collected via the water displacement method. Both gaseous and liquid products were analyzed by gas-chromatography (GC).

Table 1. Origin and characterization of different types of castor-oil

Oil feedstock	Origin	Gross Heat of Combustion (MJ/Kg)	Density (15 °C) (g/ml)	TAN Acidity (mg KOH/g)
Castor oil 1	105N	36.8366	0.9699	7.9541
Castor oil 2	Hybrid11	36.9904	0.9656	9.0814
Castor oil 3	Hybrid12	37.1284	0.9664	18.9626
Castor oil 4	Hybrid13	36.9766	0.9670	19.6668
Castor oil 5	Hybrid14	36.7637	0.9690	12.5468

Effect of co-processing different amounts of Castor oil 1 was studied applying the optimum cracking conditions and the selected comercial catalyst. Finally, the effect of different type of castor-oil quality (Castor oils 2-5) on the conversion and selectivity during cracking experiments was further investigated.

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UTILIZATION OF BIODIESEL PRODUCTION BY-PRODUCT: LIQUID PHASE TRANSFORMATION OF GLYCEROL TO ACROLEIN

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The idea of covering the energy demand from some renewable sources becomes more and more popular, so the biodiesel production has increases nowadays [1]. However, there is a problem accompanying this process, namely the increase of the production of glycerol as a by-product, which can cause environ-mental and economical problems, as well. The effective utilization of this by-product will be a key issue to promote the biodiesel commercialization. Consequently the study of chemical transformation of glycerol to other valuable chemicals has a new renaissance today [2].

One of the possibilities is to perform an acid-induced dehydration of glycerol to acrolein. Acrolein is an important chemical intermediate, so it is very important to develop a sustainable and cost-effective production route via glycerol from biodiesel, which offers an alternative for the presently dominating petrochemical process based on propylene.

The dehydration of glycerol to acrolein became a relatively well studied subject recently, when the biodiesel production started to grow. However, most of these works applying drastic conditions, e.g. the dehydration of glycerol in sub- and supercritical water [3] and /or gase phase processes [4,5]. However in the oil industry the liquid phase processes are preferred over the gase phase processes.

Our the final goal was to develop a liquid phase process for the dehydration of glycerol, at the same time to introduce an environmentally benign production of acrolein. For our study relatively mild conditions were selected and a new heterogeneous catalyst was used, which could replace the very corrosive sulfuric acid in this process. We have anchored the phosphotungstic acid hydrate on Al_2O_3 support. The prepared catalyst was characterized by FT-IR spectroscopy and was applied in the liquid phase dehydration of glycerol. Our results show that the dehydration reaction has not started below 240 °C, and it seems that a good acrolein production needs at least 280 °C or even higher temperature. In other words, the most difficult problem in the laboratory and in the industry, to find a good, neutral solvent with a high boiling point.

Applying a good acidic catalyst and a high boiling point solvent we could determine the optimum conditions for the dehydration of glycerol. Using these conditions we could produce total conversion and very high (93 %) selectivity, which are the best values–according to our knowledge–so far in the literature. Meanwhile we could not observe any other dehydration products (e.g. acetic acid, acetaldehyde). At the same time our catalyst has the advantage of the heterogeneous catalysts, namely it is recyclable in several subsequent runs without any significant change in activity and selectivity.

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ORAL PRESENTATIONS

Section IV. BIO-PHOTO-/ELECTRO-CATALYTIC CONVERSION OF RENEWABLES

Bio-catalysis for chemicals production

Photo-catalysis for environmental protection

Electro-catalytic conversion of renewables

OP-IV-1

PHOTOCATALYTIC FISCHER–TROPSCH SYNTHESIS ON GRAPHENE-SUPPORTED RUTHENIUM NANOCHAINS

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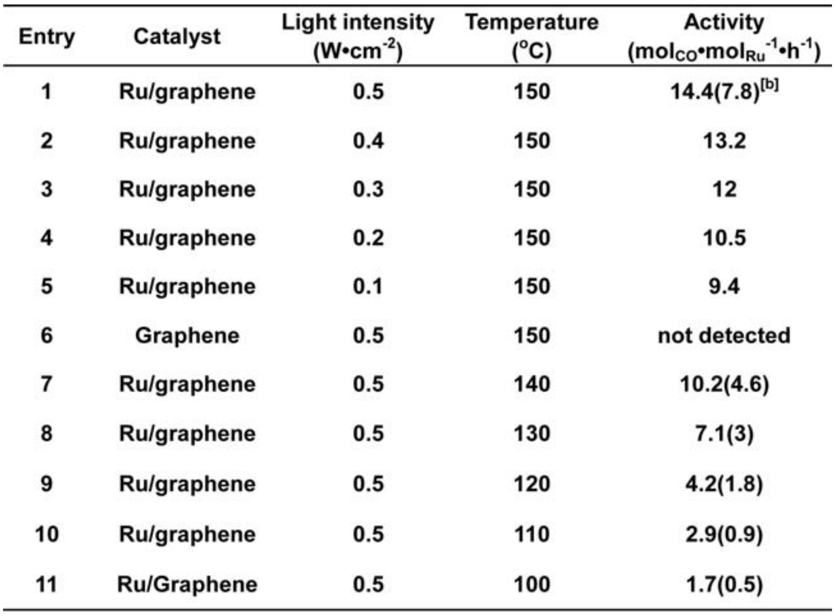
Fischer–Tropsch synthesis (FTS) converting carbon monoxide and hydrogen to liquid fuels and chemicals is becoming more and more attractive due to the increasing scarce of fossil energy [1-3]. Traditional FTS technologies are operated under high temperature ranges [4]. The high temperature operation results in evidently increase of energy consumption and CO_2 emission [5]. A photocatalytic FTS route was proposed to efficiently harvest solar energy.

The Ru/graphene catalyst was prepared by reducing ruthenium trichloride in the presence of poly(N-vinyl-2-pyrrolidone) (PVP) using 2.0 MPa H_2. TEM images show that short Ru nanochains with a diameter of 2.2 nm and length of ~10 nm are homogeneously dispersed on the graphene sheets. From the UV-vis spectra, the Ru/graphene shows stronger light absorption than pure graphene, indicating that the enhanced light absorption originates from the Ru nanochains dispersed on graphene sheets.

Table 1. Performances of Ru/graphene for PFTS under different reaction conditions[a]



Entry	Catalyst	Light intensity ($W•cm^{-2}$)	Temperature (^oC)	Activity ($mol_{CO}•mol_{Ru}^{-1}•h^{-1}$)
1	Ru/graphene	0.5	150	14.4(7.8)[b]
2	Ru/graphene	0.4	150	13.2
3	Ru/graphene	0.3	150	12
4	Ru/graphene	0.2	150	10.5
5	Ru/graphene	0.1	150	9.4
6	Graphene	0.5	150	not detected
7	Ru/graphene	0.5	140	10.2(4.6)
8	Ru/graphene	0.5	130	7.1(3)
9	Ru/graphene	0.5	120	4.2(1.8)
10	Ru/graphene	0.5	110	2.9(0.9)
11	Ru/Graphene	0.5	100	1.7(0.5)

[a] Catalytic tests were performed over 30 mg Ru/graphene (containing 0.2 mmol Ru) under 2.0 MPa H_2 and 1.0 MPa CO and the irradiation of a 300 W Xe lamp, whose wavelengths range from 400 to 800 nm. The catalytic activity is represented by moles of CO converted to hydrocarbons per mol of Ru per hour. [b] Values in parentheses show the catalytic activity without irradiation (dark reaction).

The PFTS process of Ru/graphene was carried out under 2.0 MPa H_2, 1.0 MPa CO and the irradiation of a 300 W Xe lamp (400-800 nm) at 150 °C. The reaction results are summarized in Table 1. The Ru/graphene exhibits high photocatalytic activity for FTS. The conversion of CO over the Ru/graphene is 43 % and the activity is 14.4 $mol_{CO}•mol_{Ru}^{-1}•h^{-1}$. Without irradiation (dark reaction), the catalyst under the same temperature and pressure only shows an activity of 7.8 $mol_{CO}•mol_{Ru}^{-1}•h^{-1}$, indicating that the irradiation of visible light can significantly enhance the intrinsic catalytic ability of Ru/graphene for FTS. The highest activity in visible light range is observed in 400-500 nm, where the Ru nanochians strongly absorb the light. The bound electrons in Ru nanochains can absorb irradiation light via interband transitions and become energetic. These energetic electrons can transfer to reactant molecules and promote the chemical transformations between these molecules, therefore high temperature for promoting the reaction can be avoided.

The selectivity of CO_2 over the catalyst is less than 1 mol %. The hydrocarbons are the main products with a selectivity of 86.9 wt %, whereas the selectivity towards oxygenates (mainly alcohol) is 13.1 wt %. Among the hydrocarbons, C_{5+} hydrocarbons take the majority (81.7 wt %) of the products, and only 2.6 wt % of methane was formed. It is notable that the more useful olefins represent 56.4 % of the whole C_2-C_4 hydrocarbons (gaseous products), suggesting that the Ru/graphene is a desirable catalyst for light olefins in the gaseous range. The selectivities of different hydrocarbon products follow the Anderson–Schulz–Flory (ASF) distribution, with a growth factor (α) of hydrocarbon products of 0.78.

Since the nonplasmonic metals (such as Ru) have been widely used as the catalysts for various reactions, the reported discovery may significantly broaden the applications of catalytic processes driven by light.

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THE SYNTHESIS OF CATALYSTS BASED ON $Cd_{0.3}Zn_{0.7}S$ DOPED BY TRANSITION METALS FOR PHOTOCATALYTIC HYDROGEN PRODUCTION UNDER VISIBLE LIGHT

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Hydrogen as environmental friendly and high-energy fuel has attracted attention all over the world for the last decade. Photocatalytic water splitting under the visible light is a very promising and interesting method of the hydrogen production. In order to achieve higher efficiency for photocatalytic water splitting many researchers in this field have involved electron donors as “sacrificial agents”, which can react irreversibly with the formed oxygen or photoinduced hole [1]. In this research we chose Na_2S/Na_2SO_3 system as an inorganic electron donor for the H_2 production. CdS was the first photocatalyst to be employed in H_2 production by irradiation of its aqueous solutions with visible light using sulfide ions as electron donors. CdS is characterized by a band gap of 2.4 eV, and the positions of its valence and conduction bands are suitable for the photocatalytic decomposition of water. A possible ways of enhancing the photocatalytic activity of cadmium sulfide are to develop solid solutions like $Cd_{1-x}Zn_xS$ and doping by different metals, e.g. nickel and copper [2].

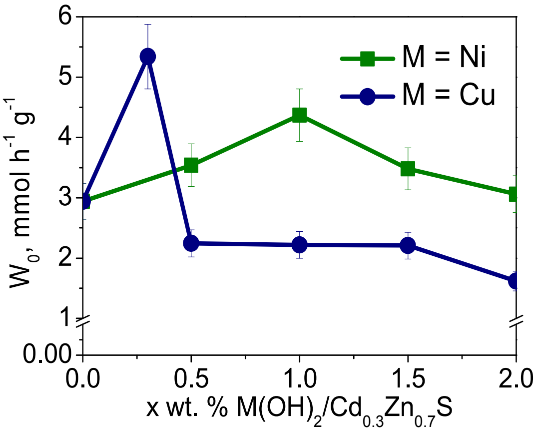

Fig. 1. The photocatalytic activity of $Cu(OH)_2/Cd_{0.3}Zn_{0.7}S$ and $Ni(OH)_2/Cd_{0.3}Zn_{0.7}S$ samples

In this research, the influence of CuS, NiS, $Cu(OH)_2$, and $Ni(OH)_2$ deposition on the photocatalytic properties of $Cd_{0.3}Zn_{0.7}S$ was investigated. The activity of $CuS/Cd_{0.3}Zn_{0.7}S$ was shown to exceed that of $NiS/Cd_{0.3}Zn_{0.7}S$ photocatalysts likely

because of the more favorable heterojunctions. Also hydrogen can be produced by catalytic cycle realized on $CuS/Cd_{0.3}Zn_{0.7}S$ photocatalysts. The highest photocatalytic activity (3.52 mmol g^{-1} h^{-1}) was possessed by 1 mol % $CuS/Cd_{0.3}Zn_{0.7}S$ [2]. Fig. 1 represents dependence of the rate reacion on photocatalyst composition $M(OH)_2/Cd_{0.3}Zn_{0.7}S$, M = Cu or Ni. The most active sample are 1 wt. % $Ni(OH)_2/Cd_{0.3}Zn_{0.7}S$ (4.04 mmol g^{-1} h^{-1}) and 0.3 wt. % $Cu(OH)_2/Cd_{0.3}Zn_{0.7}S$
(5.34 mmol g^{-1} h^{-1}). $Ni(OH)_2$ is known to be reduced to Ni^0 which can produce hydrogen from protons under visible light irradiation. Also $Cu(OH)_2$ can be reduced to Cu or Cu_2O. The last one is the semiconductor, so this system may be active because of heterojunctions between Cu_2O and $Cd_{0.3}Zn_{0.7}S$.

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OP-IV-3

GUIDELINE OF α-PINENE TO VALUE-ADDED PRODUCTS USING BIOCATALYTIC TOOLS

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In the era of renewable carbon sources as a key element in biorefinery, we know of only biomass alternative for the replacement of fossil resources. Recently investigations demonstrated both terrestrial and marine environments contain important renewable carbon sources represented often by monoterpenoid compounds (monoterpenes).

In this study, biocatalytic oxidation of α-pinene designed in varied configurations has been investigated for the production of value-added products for flavors, pharmaceuticals, perfumery and food industry as well as the precursors applied in the pesticides and polymeric industries (e.g. α-pinene oxide, verbenol, pinanediol, camphene, campholenal) (fig. 1).

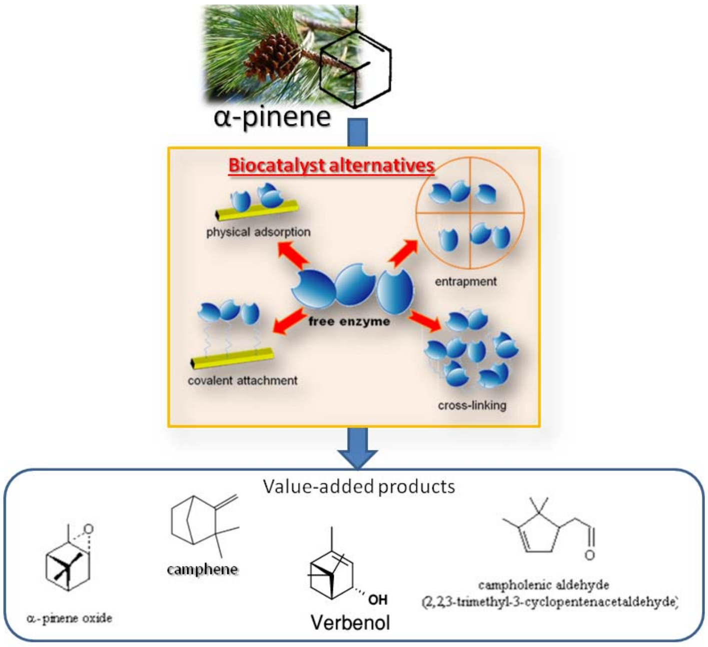

Fig. 1. Different designs for α-pinene valorization

Biocatalysts were constructed as lipase enzyme absorbed/entrapped/cross-linked leading to the specific configurations. The immobilization approaches are detailed in the previous papers [1,2].

Biocatalytic oxidation of α-pinene was performed in the mixture of substrate and oxidation agent (1:1 = α-pinene:H_2O_2/UHP) catalysed by lipase enzyme (50 mg/mL). The reaction was developed in ethyl acetate for 24 h under room temperature. Then, the reaction phases were separated by centrifugation. The supernatant was further frozen and extracted with pentane. The evolution of the biocatalytic process was followed based on GC-MS/FID analysis of the reaction products.

Lipase enzyme from *Aspergillus niger* source was immobilized leading to varied configurations (e.g. absorption, entrapment, covalent and cross-linking). The biocatalysts were tested; the results are presented in table 1. Enzyme immobilization using the entrapment approach allowed to improve the α-pinene conversion and moreover to concentrate the selectivity onto verbenol production. The other biocatalyst configurations behaved similar between them in term of selectivity leading to α-pinene oxide as dominant product next to verbenol, camphene, campholenal. All of the experimental results will be detailed and correlated to the corresponding biochemical processes during the conference presentation.

Table 1. The effect of biocatalyst design on the biochemical route of the α-pinene oxidation process. (CLEA-cross-linked enzyme aggregates and CLEMPA–cross-linked enzyme aggregates onto magnetic particles)

biocatalyst	**Conversion (%)**	**Selectivity (%)**			
		α-pinene oxide	camphene	verbenol	campholenic aldehyde
Free lipase	15.30	57.61	2.09	1.04	3.12
Adsorbed lipase	13.25	43.21	3.20	2.21	4.35
Covalent attachment of lipase	10.50	47.90	2.34	10.75	3.21
Entrapped lipase	22.58	26.34	1.36	21.00	1.67
CLEA	27.06	35.31	0.38	3.06	6.53
CLEMPA	9.61	42.37	0.89	3.06	8.20

Biocatalytic system for α-pinene valorization had been developed for production of value-added products, especially α-pinene oxide and verbenol.

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OXIDATIVE DEGRADATION OF METHYL ORANGE CATALYZED BY LAB PREPARED NICKEL HYDROXIDE IN AQUEOUS MEDIUM

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This study is focused on oxidative degradation of Methyl Orange, a common azo dye, catalyzed by nickel hydroxide in aqueous solution. Sodium hypochlorite, sodium hydroxide and nickel sulfatehexahydrate in distilled water were used as starting material for preparation of nickel hydroxide. Pyrex glass batch reactor was used to study the effect of various conditions like temperature, concentration, agitation, catalyst dose on catalytic degradation of Methyl Orange in aqueous medium. Experimental data was subjected to kinetics analysis using Curve Expert software. Degradation reaction was taking place according to Langmuir-Hinshelwood mechanism. According to this mechanism the reactants adsorb at the surface of catalyst in first step followed by reaction between adsorbed reactants in second step. Adsorption of Methyl Orange on surface of catalyst followed Langmuir adsorption isotherm. Apparent activation energy, true activation energy, heat of adsorption, entropy and free energy of reaction were determined.

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SCHOOL OF YOUNG SCIENTISTS

Section I. CATALYSIS IN DENDROCHEMISTRY FOR VALUABLES PRODUCTION

MECHANOCHEMICALLY-FABRICATED FUNCTIONAL MATERIALS FOR XYLOSE-TO-FURFURAL TRANSFORMATION

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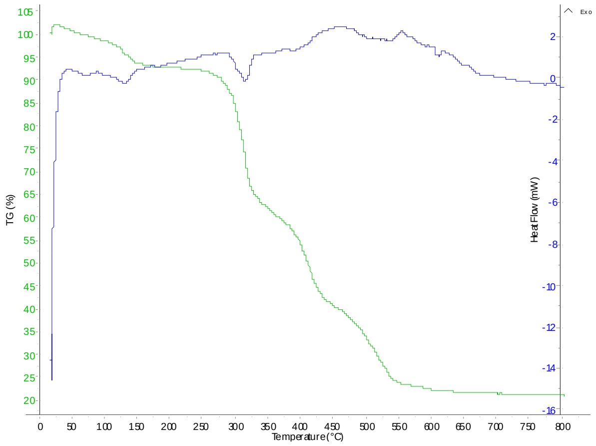
Over the last decade, there has been a growing interest in the potential of lignocellulosic biomass as an alternative for petroleum resources; this is because of its abundance as a feed stock and its carbon neutrality. Industrially, the conventional way lignocellulosic biomass is utilized results in its conversion to bioethanol, but in order to achieve full scale commercial profitability, it is imperative to generate other value added chemicals from lignocellulosic biomass. One compound that shows a lot of promise is furfural. Furfural is synthesized by the cyclodehydration of pentose sugars and it is a strategic chemical because of its numerous possible applications in oil refining, plastics and pharmaceuticals and bio-fuel [1]. To elucidate the production process from homogeneous to heterogeneous catalysis, efforts have been made to convert xylose, an important component of hemicellulose to furfural using catalysts based on zeolites, SBA-15, clay, ionic liquids, metal halides etc.

This work is the first one to report the use of metal organic framework (MOF) as a heterogeneous solid catalyst to convert xylose to furfural. MOFs are ordered porous molecular assemblies constructed by coordination bonds, where metal atoms form the vertexes and organic polydentate molecules the linkers. MOFs can be tuned according to specific requirements by modifying the organic linker or ionic cluster [2]. To emphasize green technology and reduce use of solvents, the catalyst MOF has been prepared by ball milling process [3].

Methodical screening of various metals lead us to conclude that nickel and zinc based MOFs with trimesic acid gives best results for the xylose dehydration reaction. TGA analysis showed that stability of the MOFs is maximum 250 °C. The initial weight loss till 100 °C is due to loss of unreacted products or water from inside the pores. Weight loss after 250 °C is due to decomposition of organic linker.

OP-I-YS-1



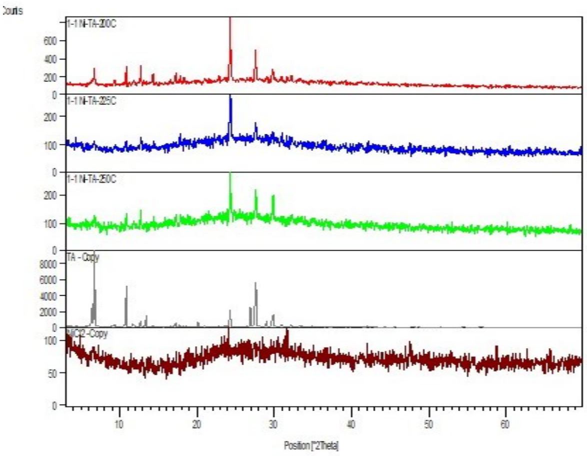


Figure 1. TGA of Ni-MOF calcined at 200 °C

Figure 2. XRD of developed MOFs

The XRD data indicates that crystallinity of MOF is better when calcined at lower temperature, since the ligand structure undergoes transformation at higher temperature.

Till date maximum furfural yield and selectivity of 60 % and 70 % respectively has been achieved along with xylose conversion of above 85 % when reaction was conducted at 170 °C for 180 minutes in presence of Ni-MOF. Zn-MOF also gave 60 % yield at same operating conditions.

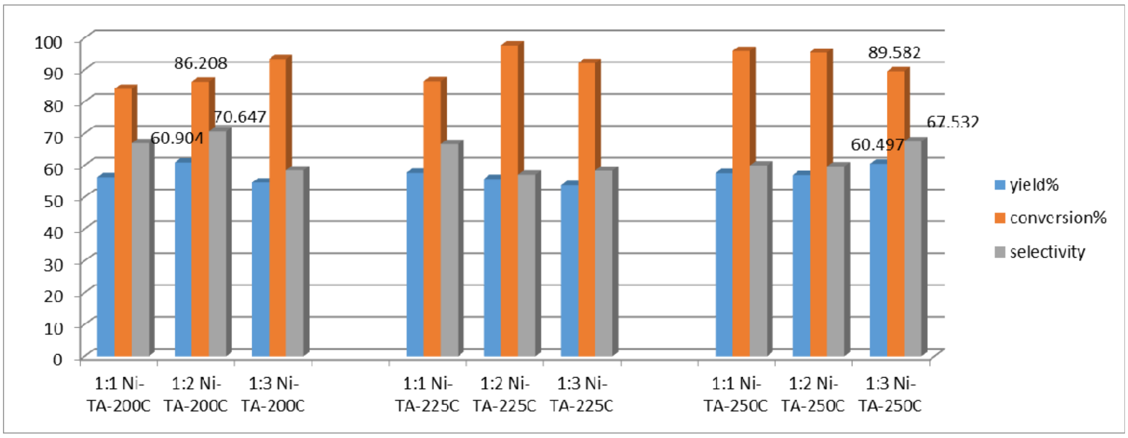


Figure 3. Chromatogram result for Ni-MOF

The catalyst could sustain three runs of reactions while giving similar yield of 60 % furfural. Micron sized rod shaped and star shaped Ni-MOFs and cubic shaped Zn-MOFs could be synthesized by ball milling process. The surface metal loading varied from 4-10 % by mass.

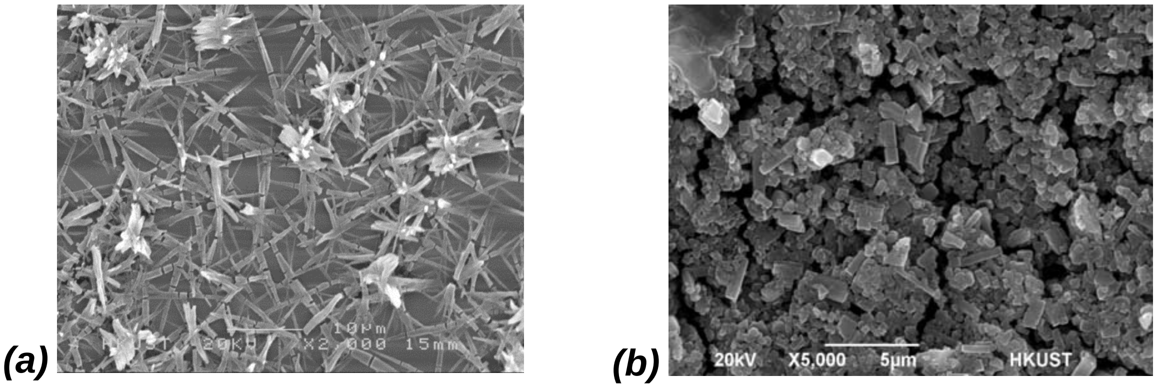


Figure 4. (a) Star shaped Ni-MOF and (b) Cube shaped Zn-MOF

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OP-I-YS-2

CATALYTIC WET AIR OXIDATION OF D-GLUCOSE

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Catalytic oxidation of saccharides performed with air under mild condition is taking interest because it is more environmental friendly than stoichiometric oxidation with mineral oxidizing agents. With this approach, it is possible to obtain fine chemicals and intermediates for further transformations in cheaper and cleaner processes. The present investigation focused on the formation of gluconic acid and D-saccharic acid as products of D-glucose oxidation; gluconic acid presents wide applications in both food and pharmaceutical industry [1], while D-saccharic acid has used as key intermediate in the formation of adipic acid [2].

Platinum was selected as the active phase for the supported catalyst while several types of support were investigated for the conversion of D-glucose. All catalysts were prepared with wet impregnation method and their surface areas were determinates with a Tristar II (Micrometrics Instrument Corporation) surface area and porosity analyzer (*tab. 1*). Catalytic wet air oxidation of D-glucose water solution (1 wt %, Sigma-Aldrich) was tested in a 300 ml batch stirred reactor (Berghof BR-300) at 353 K. In a typical experiment, the reaction tests were carried out for 5 hours; the time of reaction was selected in order to maximize D-saccharic acid yield. In all cases, 50ml of solution with a specific amount of catalyst were employed in order to establish a metallic charge of 1 mol %. An air pressure of 5 bar and a temperature of 353 K were chosen as standard conditions for the tests, since higher partial pressure of oxygen did not significantly increase the yields to organic acids (*fig. 1*), and higher temperature increased the cracking of saccharide molecules.

Gas product analysis was carried out by using a Micro GC (SRA instruments) equipped with a thermal conductivity detector (TCD); a Molsieve 5A column with Argon as gas carrier, was used to analyze hydrogen, oxygen, nitrogen and carbon monoxide. Moreover, carbon dioxide were also quantified in a PPU column with Helium as gas carrier. Liquid products were characterized by high performance liquid chromatography (Shimadzu Corporation) equipped with a Rezex ROA H+ organic acid column; organic acids were quantified with a Photodiode Array Detector (λ = 212 nm). The performances of catalysts are summarized and reported in *table 1*.

Table 1: List of catalysts prepared, SSA of samples, and conversion and yields obtained in the oxidation of D-glucose; GluA (gluconic acid), SacA (D-saccharic acid)

Catalyst	Surface Area (m^2/g)	Conversion (mol %)	Yield (mol%)	
			GluA	**SacA**
Blank test	-	5,3%	0,6%	1,9%
Pt / SiO_2	18,0	5,6%	0,8%	1,6%
Pt / SBA-15	711	17,3%	9,4%	2,0%
Pt / Al_2O_3	172	59,9%	26,2%	10,6%
Pt / C	111	76,2%	47,6%	8,3%
Pt / TiO_2	127	20,7%	16,5%	2,2%

The highest yields to the desired compounds were achieved with Pt/C (carbon nanopowders <100 nm particle size), even if the sample based on Pt supported on the mesoporous silica SBA-15 exhibits the highest value of BET surface area.

Furthermore, a basic environment for the reaction over the Pt/C catalysts was settled by using a $NaHCO_3/Na_2CO_3$ buffering system with a characteristic pH of 10. In this case conversion rose up to 100 % and the molar yield of D-saccharic acid achieved 28,0 %; Nevertheless the molar yield of gluconic acid decrease to 31,4 %, suggesting that gluconic acid could represent an intermediate compound in the formation of D-saccharic acid.

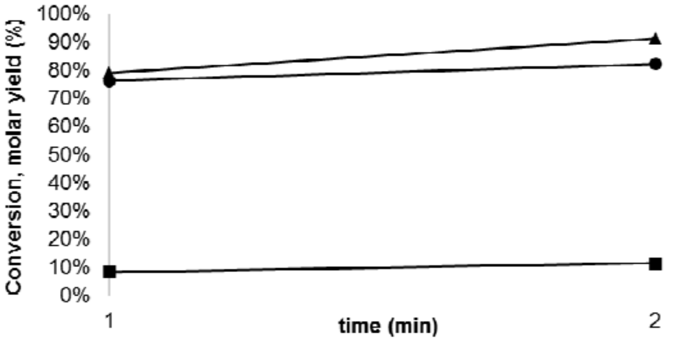

Figure 1: Change in products distribution at higher oxygen partial pressure for the oxidation of D-glucose using Pt/C. (●) conversion of D-glucose; (▲) gluconic acid and (■) D-saccharic acid yields

Further improvements of the system, as bimetallic catalysts and alternative metal or support, have been investigated in order to maximize d-glucose conversion and increase selectivity towards glucaric acid and D-saccharic acid in aqueous mean. Leaching and catalyst deactivation were also investigated.

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OP-I-YS-3

CATALYTIC WET AIR OXIDATION OF LIGNIN OVER PEROVSKITE-TYPE OXIDES AS CATALYSTS

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The overcoming of a fossil fuels based economy is one of the main challenges that the human kind has to face in the 21st century in order to thrive on long term. In this sense, the development of an efficient model of integrated biorefinery based on renewable biomasses seems to be fundamental to ensure a sustainable production of fuels and chemicals. Lignocellulosic materials are approximately constituted by two thirds of cellulose and hemicellulose while another third is represented by lignin. The composition is strictly related with the origin of the material; in particular, processes based on second generation biomasses such as agricultural residues and non-edible vegetables, should be effective on organic substrates characterized by higher percentages of lignin if compared with the so-called energy crops. Generally, cellulose and hemicellulose are hydrolyzed into the corresponding sugars constituting their structures and then transformed mainly into ethanol, while the lignin fraction is considered as a waste and it is mostly burned to produce energy or steam. However, despite years of efforts, the development of a commercial plant for biomass-to-biofuel conversion is still economically tricky. In order to achieve the economic sustainability of these processes, one of the solutions is to couple the production of fuels with high-added value chemicals and secondly exploit everything offered by the biomass to achieve cost effectiveness [1].

In this sense, the aim of our work has been to take a residue, steam exploded lignin derived from wheat straw, and to transform it firstly into substituted phenols and secondly into dicarboxylic acids through an oxidative process with air as first oxidant agent. Perovskite-type oxides have shown high oxidative activity in similar processes [2,3], therefore several perovskites have been prepared through the solution combustion synthesis (SCS) and tested in the oxidation of lignin. The experiments have been carried out in a pressurized 50 ml batch reactor loaded with water as solvent. The process run for 1-4 hours with temperatures ranging from 200 to 250 °C and air pressure between 30 and 50 bar, showing lignin dissolution up to 80 %. A μGC analyzer has been adopted to monitor the undesired production of CO_2, while the reaction mixture is extracted with ethyl acetate to separate the aromatic compounds from the dicarboxylic acids which remain in the acqueous phase; afterwards the species have been quantified via GC-MS and ionic chromatography. Catalysts have been characterized through XRD, TPO and FE-SEM analysis. Best catalytic performances have been achieved with $CeFeO_3$ and $LaFeO_3$ catalysts, that showed guaiacol, 5-(hydroxymethyl)furfural, vanillin and acetovanillone as main compounds concerning the organic phase, and succinic acid, glutaric acid and adipic acid as the main components of the aqueous phase. Even though the yields are limited, the novelty of the process is the generation of saturated C4, C5 and C6 dicarboxylic acids not observed in similar processes, in past investigations. These results are in contrast with the hypothesis of the formation of quinone intermediates followed by aromatic ring cleavage to provide unsaturated dicarboxylic acids [5]. Further work is on-going to enhance the performances of the process and to elucidate the reaction mechanism.

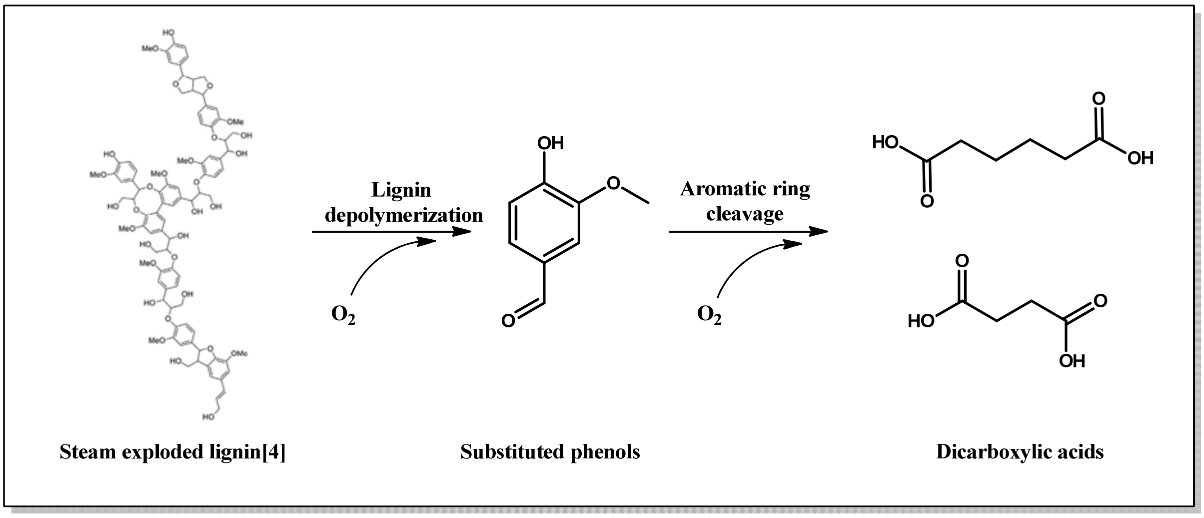

Fig. 1. Lignin transformation steps into dicarboxylic acids

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Acknowledgements

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Section II. BIOMASS DERIVATIVES IN PETROCHEMISTRY

KINETIC MODELLING OF CATALYST USED IN METHANATION OF CO_2 FOR POWER-TO-GAS APPLICATIONS

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In Power-to-Gas concept, surplus electricity is converted to hydrogen by water electrolysis and subsequently, it is converted with CO_2 from exhaust gases (renewable or not renewable sources) to synthetic natural gas. The aim of this study is to develop kinetic models which describe the behavior of Ni-based catalysts used in methanation of CO_2 at different operation conditions. Most of the literature about kinetics for methanation of CO_2 focus on the temperature range of 200-300 °C which is far from real operation conditions in a reactor [1], [2]. The novelty of this study is to model the catalyst behavior at the range of temperatures with high catalytic activity (300-600 °C) where the runaway of the reaction temperature is difficult to control. Furthermore, the kinetic models describes intrinsic properties of the catalyst such reaction and adsorption enthalpies, kinetic and adsorption constants, and activation energies of reactions and compounds involved in the process.

Experimental/methodology

A Ni-based commercial catalyst is tested in a one-tube-one-shell heat exchanger (HEX) reactor cooled by steam in order to improve temperature control in the catalyst bed (CB). Likewise, five thermocouples are placed inside the inner tube to obtain the temperature profiles in the CB which is used in the kinetic modelling. The catalyst is crushed and sieved to a particles size from 200 to 300 μm to reduce external and internal mass transfer limitations. Subsequently, the catalyst is diluted to 50 vol-%. with SiC to decrease temperature gradients in the catalyst bed. The analysis of the reaction products is performed by gas chromatograph using TCD and FID detectors. Kinetic experiments are performed at a

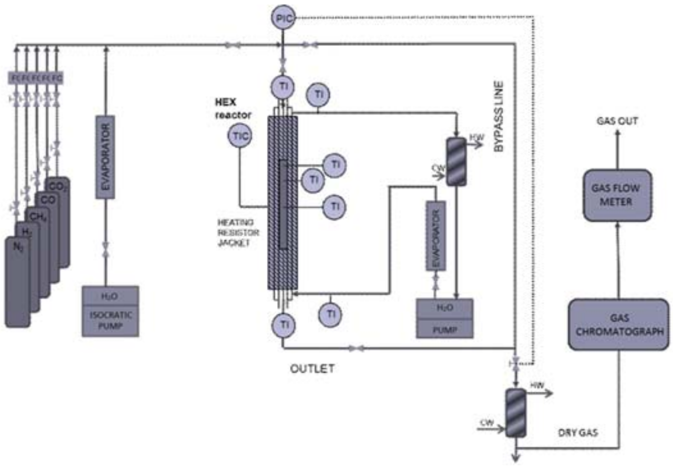

Fig. 1: Experimental set-up

temperature range of 200-600 °C, at H_2/CO_2 ratios from 3.5 to 4.5, pressures from 1 to 15 bar, and different feed flow rates without gas dilution. Fig. 1 shows the experimental set-up.

Results and discussion

The results of the experiments are used to fit the different parameters of the models. Both empiric-based models and reaction-mechanism-based models are obtained for methanation of CO_2 process. The empiric models are power-law models based on the equilibrium of both methanation of CO_2 (1) and WGS reactions (2).

$$r_{M\_CO_2} = k \cdot p_{CO_2}^{a} p_{H_2}^{b} \left[1 - \frac{p_{CH_4} p_{H_2O}^{2}}{K_{eq} \cdot p_{CO_2} p_{H_2}^{4}} \right] \quad (1)$$

$$r_{rWGS} = k \cdot y_{CO_2} y_{H_2} - k^{-1} \cdot y_{CO} y_{H_2O} \quad (2)$$

The mechanism-based models are Langmuir-Hinshelwood (LH)-type. These rate equations can be very complex but the best fit to experimental data can be found by them. Furthermore, LH models are more appropriate to represent the catalyst behavior in equilibrium limited reactions.

$$r_{M\_CO_2} = \frac{k \cdot p_{CO_2}^{a} p_{H_2}^{b} \left[1 - \dfrac{p_{CH_4} p_{H_2O}^{2}}{K_{eq} \cdot p_{CO_2} p_{H_2}^{4}} \right]}{\left(1 + K_{CH_4} \dfrac{p_{H_2O}}{p_{H_2}^{0,5}} + \sqrt{K_{H_2} p_{H_2}} + K_{CO_2} p_{CO_2}^{0,5} \right)} \quad (3)$$

Sixty operating points are performed in order to calculate 4 to 8 floating parameters in the models. Moreover, the operating points are as heterogenous as possible to produce outlet composition of the reactor in equilibrium and non-equilbrium state even at high temperatures and pressures.

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Acknowledgements

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TOLUENE OXIDATION KINETICS OVER ZrO_2-BASED GASIFICATION GAS CLEAN-UP CATALYSTS

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Gasification of biomass combined with effective catalytic gas cleaning is an attractive way to produce renewable energy as well as syngas that can be further converted into liquid biofuels or chemicals [1-2]. ZrO_2-based catalysts have been proven to remove the undesired tar molecules successfully when an appropriate amount of oxygen is added to the gasification gas [2-3]. Detailed knowledge of the tar oxidation mechanism over ZrO_2-based catalysts needs to be established in order to optimize the performance and to ensure a high-quality product gas. In our previous study, it was tentatively discovered by in situ DRIFTS that oxidation of toluene (a tar model compound) takes place at 300-600 °C, yields four products (CO_2, H_2O, CO and H_2) and the key intermediate is a surface benzyl species [4]. As a continuation, this work focuses on toluene oxidation following the surface reaction in a temperature-programmed mode. The aim of this work is to provide toluene oxidation kinetics over ZrO_2-based gasification gas clean-up catalysts.

ZrO_2, Y_2O_3-ZrO_2 and SiO_2-ZrO_2 were calcined at 800 °C for 1 h, pressed into pellets, crushed and sieved to the particle size of 0.25-0.42 mm. The TPSR (temperature-programmed surface reaction) experiments were performed in an Altamira AMI-200R catalyst characterization system with an on-line Hiden QIC-20 mass spectrometer. The samples (100 mg) were calcined at 600 °C for 2 h (5 vol-% O_2/He), cooled down to 200 °C (2.5 vol-% O_2/He) and flushed with helium for 1 h. Toluene (715 ppm in He) and oxygen (5 vol-% in He) were fed to the samples at 200 °C for 2 h, followed by heating to 600 °C (6.7, 10 or 15 °C/min) and stabilization (30 min). The total gas flow rate was 50 cm^3/min and O_2-toluene feed ratio 9.9 (≈1.1 x theor. total oxidation ratio).

The kinetic model was postulated based on thorough data analysis. The conversion of oxygen started at slightly higher temperatures than that of toluene indicating the presence of adsorbed surface species originating from toluene. Therefore, the formation of the surface benzyl species (reaction 1) was considered to be the first step, in accordance with our previous findings [4]. Since no products containing an intact benzene ring were observed, next kinetically relevant step involves the decomposition of the benzene ring. An approach to explain the observed reaction dynamics is a hypothesis where the benzyl species undergoes a 'fragmentation' into five -CH and one -C_2H_2 subunits (reaction 2). Furthermore, the shape-similarity of CO_2 and H_2O formation curves suggested that these products were formed in the same reaction (reaction 3). Similar reasoning was applied for CO and H_2 (reaction 4). In order to achieve the measured product ratios, the oxidation reactions of CO and H_2 (reactions 5 and 6) have to be included in the model.

C_7H_8 (g) → [C_7H_7] + 0.5 H_2 (g) (1)
[C_7H_7] → 5 [CH] + [C_2H_2] (2)
[CH] + 1.25 O_2 (g) → CO_2 (g) + 0.5 H_2O (g) (3)
[C_2H_2] + O_2 (g) → 2 CO (g) + H_2 (g) (4)
CO (g) + 0.5 O_2 (g) → CO_2 (g) (5)
H_2 (g) + 0.5 O_2 (g) → H_2O (g) (6)

The measured and modelled TPSR profiles of all the components over ZrO_2 are shown in Fig. 1. The model gave a good preliminary fit for all the components, especially for toluene. The fit for the other components will be improved by further optimizing the kinetic parameters for reactions 2-6.

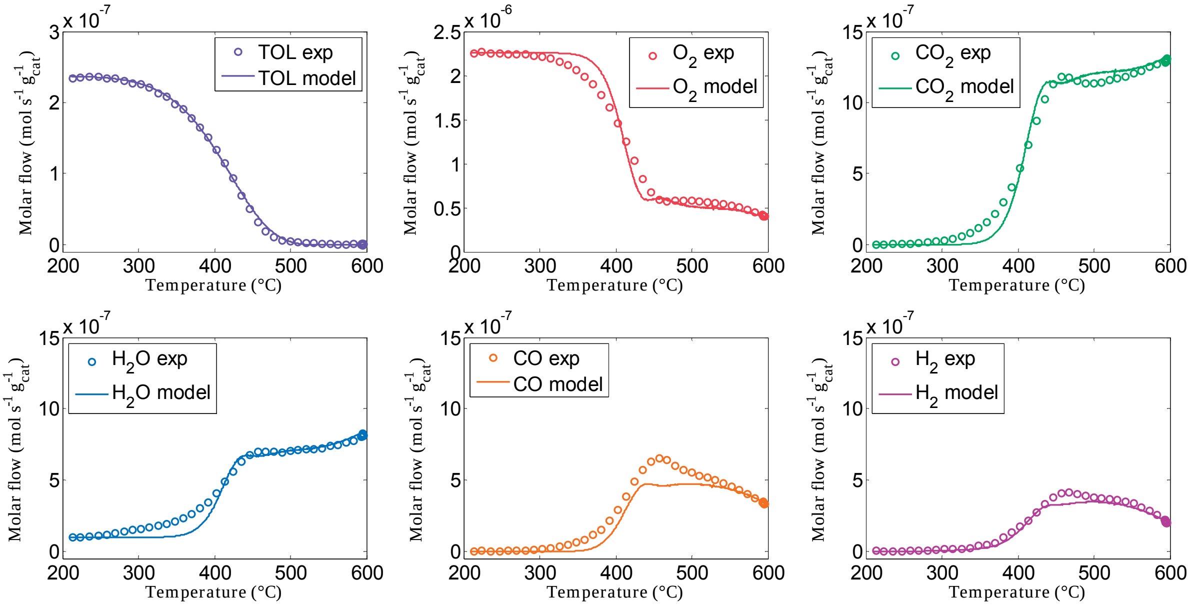

Figure 1. Measured and modelled TPSR profiles over ZrO_2, heating rate 6.7 °C/min

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CARBON DIOXIDE METHANATION FOR INTENSIFIED REACTORS

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The present work is related to the development of sustainable energy systems through the Power-to-Gas concept. The main objective is to utilise renewable hydrogen and carbon dioxide to produce methane for storage in the natural gas infrastructure.

Multitubular fixed-bed is the state-of-the-art reactor for methanation established at industrial scale. Catalytic pellets commonly loaded in this type of reactor involve poor heat transfer and high pressure drop that result in inefficient processes. In order to overcome those limitations, VTT is developing an intensified reactor concept based on heat-exchanger (HEX) reactor and novel catalyst deposition methods by washcoating and ALD-nanocoating.

The aim of this work was to determine the suitability of these novel catalysts for CO_2 methanation, and the optimal operation conditions that favour their performance. Pursuing this objective, washcoated and nanocoated catalysts were tested in laboratory scale, and compared with conventional packed-bed catalysts.

Experimental

The reactor design aimed for efficient heat removal and compact size. The reactors were tubes of alloy Inconel 6XI, 29 mm long, with inner diameter of 4 mm and 2 mm thick reactor wall. The reactors were loaded with nickel-based catalysts on metal oxide support. Methanation was performed at three different temperatures (350, 400 and 500 °C), with three different flow rates at each temperature (0.7, 1 and 1.3 ln/min), H_2:CO_2 = 4 ratio, and at atmospheric pressure. Exceptionally, some of the catalysts were tested at different temperature and flow rate set points. The average length of the runs was approximately 30 minutes.

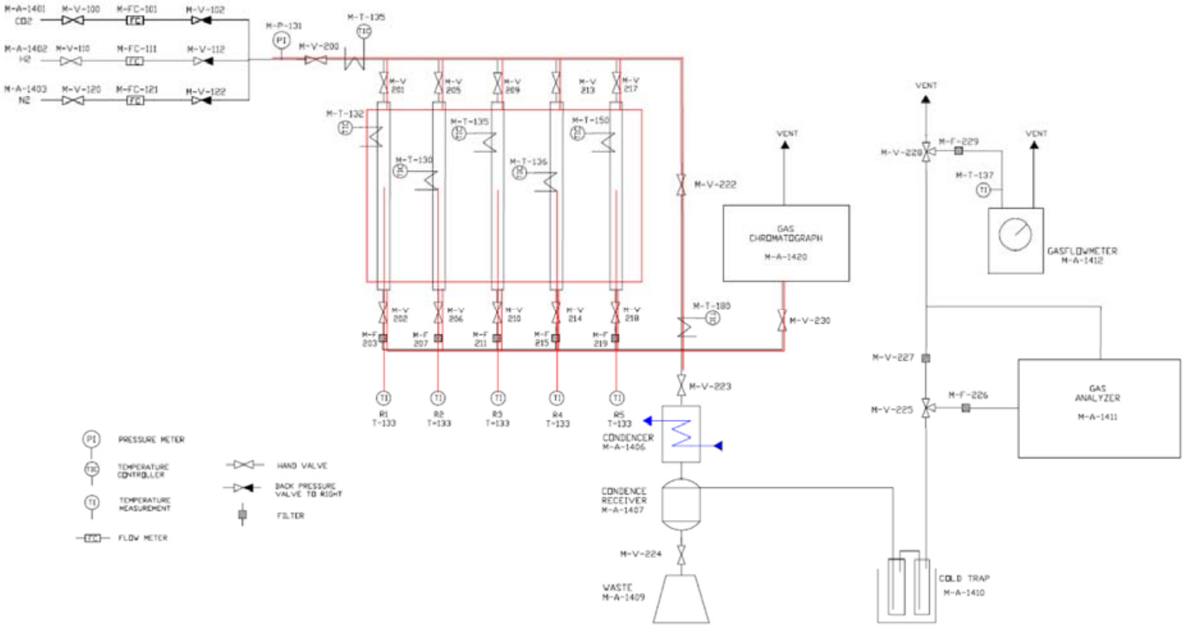

Figure 1. Methanation process diagram (by Mari-Leena Koskinen-Soivi, VTT)

Results and Discussion

The catalyst bulk density of washcoated reactors was much lower than in packed-bed reactors. As a result, the washcoated catalyst worked better due to efficient heat transfer and temperature control. Consequently, the selectivity and yield of methane was negatively affected.

The most outstanding results were obtained with the washcoated catalysts. Carbon dioxide conversion equal to 69 % and methane selectivity as high a 99 % were obtained over the washcoat with highest nickel content at 410 °C. Similar performance was observed in a washcoat with half of the nickel content and increased nickel loading. This catalyst exhibited good selectivity towards methane (98 %), and 69 % of CO_2 conversion at 462 °C.

Conclusions

Results with the washcoated reactors were better compared with the packed-bed reactors due to improved heat removal. However, nanocoated catalyst exhibited poor performance with low conversion and selectivity, and further catalyst development is needed. The results of methanation using washcoated catalysts encourage the development of these catalysts into scaled-up configurations.

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Section III. CATALYTIC PROCESSES FOR BIOFUELS PRODUCTION

PROMOTING THE ENHANCEMENT OF BIO-OIL DEOXYGENATION BY METAL CATION IMPREGNATION OF HIERARCHICAL ZSM-5 ZEOLITES

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New technologies are being studied in order to obtain liquid biofuels from renewable sources such as biomass. The resulting liquid obtained by pyrolysis of biomass presents inferior characteristics than commercial fuels (lower heating value, higher acidity, poorer stability,…), preventing its direct application in the current infrastructures. Thus, it is compulsory to improve its properties to be a viable alternative to current liquid fuels. There are several technologies focused on improving the bio-oil properties, being deoxygenation by catalytic vapour cracking one of the most promising ones. Due to their own porous structure and its acidic character, ZSM-5 zeolites seem to be the most effective zeolites to upgrade the characteristics of the bio-oils. Cracking and aromatization reactions are promoted at the Brønsted acid sites, favouring the production of aromatics in the upgraded liquid. A further improvement in the bio-oil properties has been obtained after incorporation of mesoporosity in the ZSM-5 zeolites. It has been reported that enhanced accessibility to the zeolite acid sites remarkably increases the production of aromatics. Another route for bio-oil upgrading entails the use of metal-loaded zeolites, where the incorporation of new active sites could lead to improved bio-oil characteristics.

The aim of this work is to further increase the deoxygenation of biomass pyrolysis bio-oils using metal-loaded hierarchical zeolites. Initially, a hierarchical zeolite ZSM-5 has been produced by desilication (NaOH treatment and HCl acid washing) of a commercial ZSM-5 (Zeolyst International Si/Al =40). Then, five different 1 wt% metal-loaded zeolites have been obtained by wet impregnation of Ni, Ga, Sn, Cu and Mg salts. Oxygen reduction, aromatic compound yield, chemical composition and fuel properties of the upgraded bio-oils have been determined and the obtained results have been related to the main properties of the metal-loaded zeolites.

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Table 1. Elemental analysis and fuel properties of different bio-oils

	Elemental analysis					Fuel properties			Deoxig. %	Coke
	C	H	N	S	O	TAN (mg KOH/g)	HHV (MJ/Kg)	Viscosity (cP)	%	wt. %
Initial	60.0	7.4	0.3	0.0	32.0	33.8	25.4	85.5	-	-
Non-catalytic	62.0	7.9	0.1	0.0	29.9	32.9	27.3	10.2	7	-
Meso HZ-40	71.9	8.1	0.2	0.0	19.8	24.1	32.5	9.6	38	18
Ga/meso HZ-40	73.6	8.0	0.2	0.0	18.1	26.9	31.8	9.2	43	16
Sn/meso HZ-40	72.9	8.0	0.1	0.0	18.9	22.8	32.2	10.1	41	18
Cu/meso HZ-40	73.0	8.0	0.2	0.0	18.7	27.9	32.3	9.6	42	15
Ni/meso HZ-40	73.6	8.1	0.2	0.0	18.2	22.0	31.8	10.2	43	23
Mg/meso HZ-40	73.7	8.1	0.1	0.0	18.1	21.2	32.0	9.8	43	16

Results have shown that upgraded bio-oil characteristics are strongly related to acidic properties of the zeolites. Thus, it can be observed in Figure 1 how the amount of Brønsted acidic sites is directly related to the yield of aromatic compounds. The highest aromatic yield is found for meso HZ-40, whilst the lowest for the Mg-loaded zeolite. Surprisingly, it should be pointed out that the latter solid leads to further enhancement of bio-oil characteristics in terms of oxygen content and acidity (see Table 1). This fact can be related to the promotion of deoxygenation reactions via ester formation (Figure 2). Mg cation at extraframework positions are mostly identified in this solid, which could act as active sites for the esterification of acid bio-oil compounds. Then, although aromatic production is the lowest, oxygen reduction is maximized leading to an overall improvement of bio-oil properties. Additionally, slightly lower coke deposition is observed for this solid compared to the acid hierarchical zeolite, where cracking reactions are more favoured.

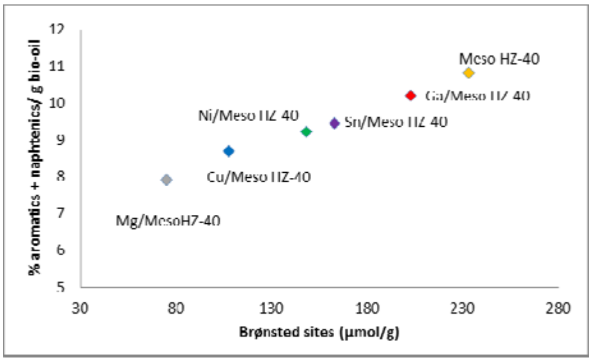

Figure 1. Influence of aromatic and naphthenic production in relation with Brønsted sites at 200 °C

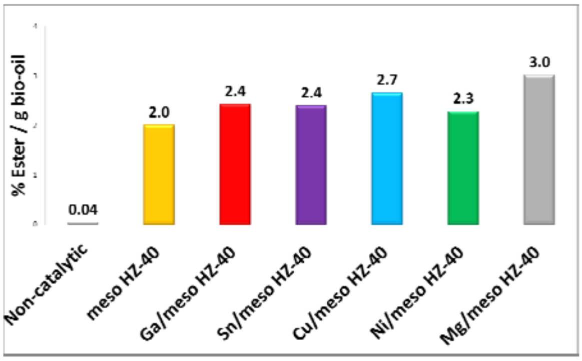

Figure 2. Ester area percentage for different upgraded bio-oils by GC/MS analysis

OP-III-YS-2

THE USE OF LOWER ALCOHOL MIXTURES FOR THE COMBINED CATALYTIC SYNTHESIS OF MONOMERS FOR THE PRODUCTION OF ELASTOMERS AND SYNTHETIC RUBBER

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Butadiene, isoprene, piperylene etc are essential petrochemicals in the rubber and plastic industry; which are mainly produced from petroleum sources. The global demand for these products is more than 9 million tones, which translates to high demand for their commercially most important polymers some of which are styrene-butadiene rubbers, polybutadiene, styrene-butadiene latex, polyisoprene, butadiene-isoprene polymers e.t.c [1-3].

The rapid development of synthetic rubber industry, depletion of oil reserves due to over dependence on fossil fuels, issues related to the environment and climate change have an adverse effect on the production of these petrochemicals and have necessitated the exploration of other alternative resources as well as research in this direction [5,6]. More interestingly, the production of shale gas as an alternative fossil fuel source currently being explored in the United States, Europe and in the near future in countries such as Poland, China, Australia will greatly impact on butadiene and isoprene production from bio-resources [3].

The catalytic conversion of ethanol-propyl alcohol mixtures with different ratios for the combined production of butadiene and isoprene was studied using Lebedev's reaction as a model. The reaction was carried out on an industrial catalyst composed mainly of Mg and Si with minute amounts of Mo, Fe, Ca, Al and Zn, at a temperature range of 370-450 °C and Flow rate – 1.2 h^{-1}.

Thermodynamic analysis of the reaction as presented in Table 1 showed a possibility of valuable C5 petrochemicals production in addition to the already known process for butadiene production. However, the reaction is characterized by the production of a large amount of by products such as ethylene, butenes, butanal, butanol hexadiene, octadiene, pentanol and other heavy organic compounds. The main reactions in the process are as follows:

OP-III-YS-2

$$C_2H_5OH + C_3H_7OH \longrightarrow \mathbf{C_5H_8} + 2H_2O + H_2$$

$$2C_2H_5OH \longrightarrow \mathbf{C_4H_6} + 2H_2O + H_2$$

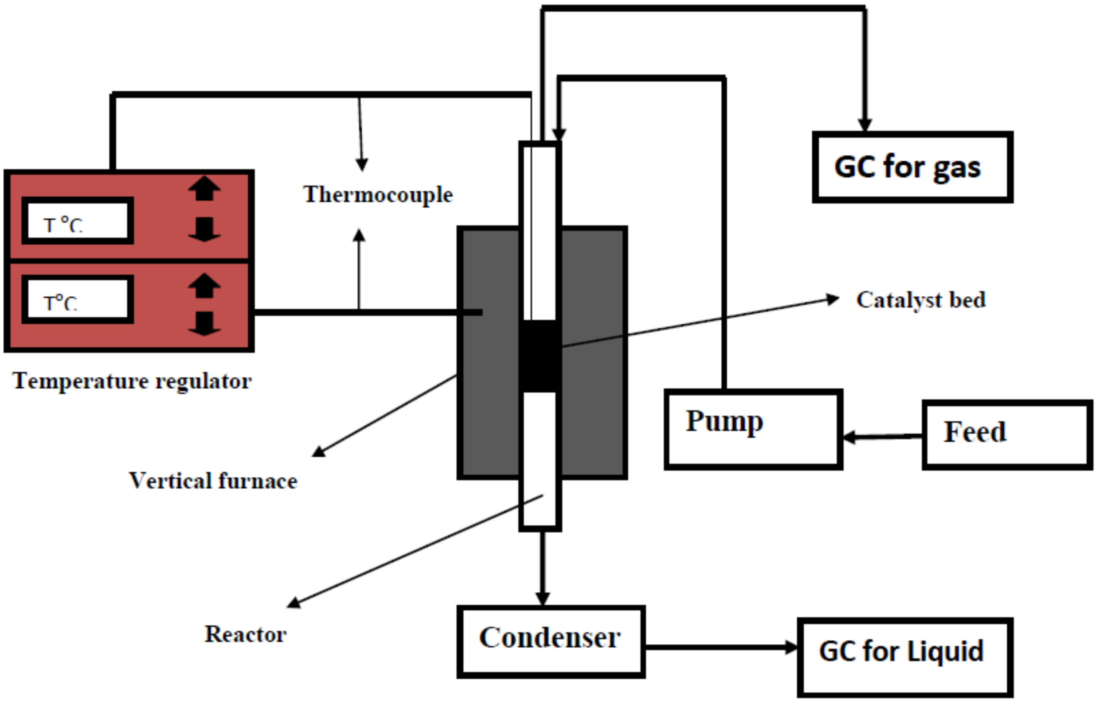

Fig. 1. The laboratory scheme for the conversion of lower alcohol mixtures into valuable petrochemicals

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PYROLYSIS OIL PROCESSING IN THE PRESENCE OF NICKEL-BASED NANODISPERSED CATALYSTS

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The product of flash pyrolysis of grinded wood, named bio-oil, is a perspective feedstock for the petrol production [1]. However bio-oil cannot substitute traditional gasoline and diesel in the internal-combustion engines owing to its lower operational properties. The main reason is the high oxygen content which is responsible for such negative properties of bio-oil as high viscosity, non-volatility, aggressivity, immiscibility with mineral oil, instability, and tendency to polymerization. The quality of bio-oil can be improved by the catalytic hydrotreatment, also known as "hydrodeoxygenation" (HDO), and other processes with hydrogen transfer such as hydrogenation, hydrogenolysis, hydrocracking and aquacracking [2]. The HDO process is carried out at high temperatures and under high hydrogen pressures (200-400 °C, 10-20 MPa). Catalytic hydrotreatment has been researched extensively with crude bio-oil and oxygen-containing model compounds used as a feedstock over Ni-Cu-based catalysts [3,4]. In the case of conventional hydroprocessing of heavy petroleum feedstocks (heavy oils, bitumens and petroleum vacuum distillation residues) the same problems arise as in the case of high viscous bio-oil. It results from the problems associated with the diffusion of molecules with high molecular weight inside the catalyst pores, which causes their blocking. At the present time an intensive research is carried out using dispersed catalysts for hydroprocessing of heavy conventional feedstocks to solve the designated problems [5]. The hydrocracking catalyst nanoparticles are formed in the reaction medium from the direct and inverse emulsions of the catalyst precursor salt solutions. This method achieves high depth of heavy feedstocks processing. Nevertheless the main disadvantage of this method is the necessity to use the significant amounts of hydrogen under the high pressure. So the employment of H_2O instead H_2 as hydrogen source can reduce cost of prior processing of heavy feedstock. The aquacracking may be promising process for bio-oil and heavy oil processing.

The aim of the present study is to compare two types of processes (hydrocracking and aquacracking) in processing of bio-oil and heavy oil. The investigation of hydrotreatment of bio-oil and its oxygen-containing model mixture was carried out in the presence of Ni-containing dispersed catalysts. These dispersed systems were prepared *in situ* during the reaction, nickel acetate being used as the catalyst precursor. Besides Ni-Cu/SiO_2 catalyst prepared by sol-gel technique and previously showed high activity in hydrodeoxygenation of O-containing compounds [3] was used in the study for comparison. The heavy oil processing has been carried out in an autoclave at 425 °C and a total pressure of 18 MPa in the presence of Ni-containing dispersed catalysts and water as a hydrogen source.

The HDO process has been carried out in an autoclave at 290 °C and a hydrogen pressure of 18 MPa. In the case of heterogeneous Ni-Cu/SiO_2 catalytic system the products of HDO process were separated from the catalyst followed by characterization of both the spent catalyst and the organic matter by physicochemical methods. CHNS-O elemental analysis, XRD, XPS and HRTEM techniques were applied to characterize the spent catalysts. The same techniques (except for XPS) were used for organic products of the hydrotreatment process.

It was observed that when using nickel acetate as the catalyst precursor the formation of active metallic nickel particles takes place under bio-oil HDO reaction conditions. Nevertheless, thus obtained dispersed catalysts possess low catalytic activity in the bio-oil HDO process unlike heavy oil aquacracking. Substantially higher activity was shown by heterogeneous Ni-Cu/SiO_2 catalysts prepared by the sol-gel method if compared with Ni-based dispersed catalysts. However, the use of this type of catalysts is expected to be promising in bio-oil hydrotreatment as it presents a convenient way of *in situ* catalyst preparation. Further investigations are targeted at searching of conditions and additives (probably variation of metal precursor) which will help to improve catalytic function of dispersed Ni-based systems.

Acknowledgements

The authors acknowledge the support of Russian Science Foundation (project №15-13-00106) and the large scale collaborative project FASTCARD ("FAST Industrialisation by CAtalysts Research and Development", EU FP7, GA № 604277).

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LIQUID PHASE FURFURAL HYDRODEOXYGENATION TO FUEL COMPONENT 2-METHYLFURAN OVER SUPPORTED METAL CATALYSTS

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Introduction

The need to produce bio-based chemicals has been expanding due to the constantly increasing energy demand and environmental concerns.[1] Valuable end products, such as 2-methylfuran (MF), can be produced from bio-based furfural. The properties of MF are superior as gasoline blending component with high research octane number (RON 131), low solubility to water (7 g/l) and high energy density [1,2].

New environmental regulations concerning waste handling prevent the use of traditional CuCr catalyst in MF production, and thus various transition metals have been studied extensively, to create new efficient substitute for CuCr catalyst [1-3]. The usual supports in furfural hydrogenation include carbon, alumina and silica.

Previous studies have achieved insufficient activities to MF production with various metal catalysts (max. yield 61 %). This study examines liquid phase furfural hydrodeoxygenation to MF with several metal catalysts, applying activated carbon as a support.

Experimental

Catalysts in this study were prepared with wet incipient impregnation method on activated carbon support. Reduction of catalyst was performed *in situ* at 250 °C and hydrogen pressure of 40 barg for one hour. Furfural hydrogenation was performed batchwise in an Autoclave Engineers 50 ml Mini-reactor at 230 °C with 2-propanol as a solvent. Samples were analyzed with gas chromatography. Unknown compounds were identified with a GC-MS.

Results and discussion

Tested catalysts included 2 % Ni/C, 2 % Cu/C, 2 %/2 % NiFe/C, 2 %/2 % CuNi/C. The yields of desired end product 2-methylfuran are presented in Figure 1.

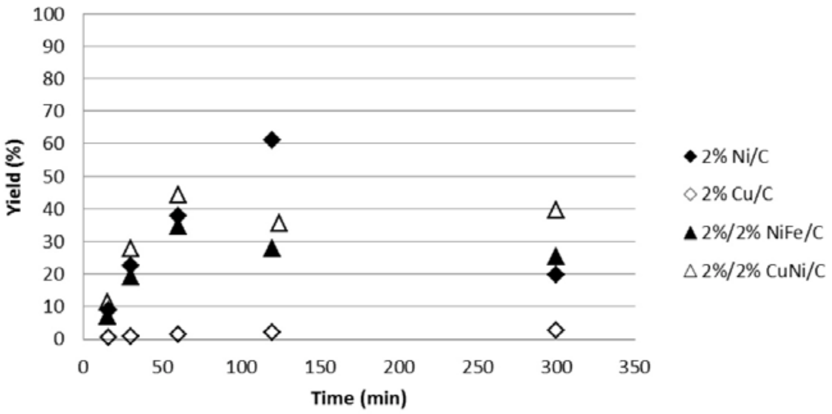

Figure 1. Yields of 2-methylfuran from liquid phase furfural hydrogenation with prepared catalysts

Results indicate that Ni/C is the most active catalyst from the prepared ones (61 % yield of MF). Cu/C reacts preferably to furfuryl alcohol and a very low yield of MF is detected. Iron has been reported to promote the furfural hydrogenation reaction towards MF, but in our experiments the yield of MF was lower over NiFe/C compared to Ni/C (61 % to 35 %). The time to achieve the highest yield was shorter on NiFe/C than Ni/C, 60 and 120 min, respectively. CuNi/C catalyst indicated medium yield of MF. Noticeable is that copper promoted the initial speed of reaction compared to pure Ni/C catalyst. The most common side products in the reactions include tetrahydrofurfuryl alcohol (THFA), furan, 2-methyltetrahydrofuran (MTHF), 2-pentanone, acetone and 2-furanmethanol acetate.

Our results indicate that very promising yields of MF can be obtained, especially with nickel on carbon support. The screening of different metal catalysts for furfural hydrodeoxygenation to MF will be extended to other metals and metal combinations. Moreover, further tuning of the investigated catalyst is expected to further improve the performance.

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POSTER PRESENTATIONS

PRODUCTION OF MULTIWALL CARBON NANO TUBES FROM TRI-METALLIC Ni-Ce-Fe CATALYST BY METHANE DECOMPOSITION IN A CHEMICAL VAPOR DEPOSITION

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This study investigates the preparation of unsupported catalysts and their application to the multi-walled carbon nanotubes synthesis .Nickel, Iron, and Cerium tri-metallic catalysts were obtained by co-precipitation reactions. The catalysts were used for the growth of multi-walled carbon nanotubes by the chemical vapor deposition method. The syntheses were conducted under methane decomposition at 900 °C. After the reaction the obtained carbon materials were characterized by scanning electron microscopy (SEM), X-ray diffraction method (XRD), Raman spectroscopy. The effect of the tri-metallic catalyst on the properties of the obtained carbon material has been described. The tri-metallic catalysts have lead to the production of multiwall carbon nano tubes.

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SYNTHESIS GAS AND ULTRA-PURE HYDROGEN CO-PRODUCTION BY DRY AND STEAM REFORMING OF FERMENTATION PRODUCTS USING HYBRID MEMBRANE-CATALYTIC REACTOR

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The original hybrid reactor consisted of Ni(Al)-Co-containing converter with integrated Pd-alloy membrane was developed. The construction allowed to carry out simultaneous processes of highly efficient dry reforming of methane (DRM) and ethanol (DRE) into syngas and in situ hydrogen separation. Removal of hydrogen decreased reaction temperature and shifted equilibrium of this processes.

Porous ceramic membrane-catalytic converters (PCMCC) produced by self-propagating high-temperature synthesis were used for investigation. Precursors included a Ni metal powder containing 5 mass % of aluminum and a cobalt oxide (II, III) powder. Components were taken in the ratios (mass %) 80 : 20 and 50 : 50, respectively.

It was demonstrated that in DRM selective hydrogen removal from reaction zone using Pd-alloy membrane allowed to increase methane conversion up to 15 % in comparison with equilibrium value. Feeding the substrate at a rate of 9 L/h and T = 550 °C hydrogen productivity was 3.7 L/h, including 50 % of ultrapure hydrogen.

It was found that in DRE selective removal of ultrapure hydrogen decreased methane containing in products and increased the total yield of hydrogen. It was determined that feeding the substrate at a rate of 30 L/h and T = 600 °C hydrogen productivity was 9 L/h, including 1.6 L/h of ultrapure hydrogen.

It was determined, that pressure increases hydrogen flux permeation through the Pd-containing membrane, causing a shift effect of the reforming processes toward the products.

Acknowledgements

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THE EARTH'S CRUST AS A CATALYTIC GENERATOR OF HYDROGEN EMISSION IN THE ATMOSPHERE AND POSSIBLE ROLE OF THIS PROCESS IN THE PHENOMENA OF OZONE LAYER DEGRADATION (EXPERIMENTAL MODELING OF HETEROGENEOUS-CATALYTIC MECHANISM OF FLUIDS TRANSFORMATION IN THE EARTH'S CRUST WITH AN EXAMPLE OF STEAM REFORMING OF METHANE WITH THE FORMATION OF HYDROGEN ON SERPENTINITE, GABBRO AND ASBESTOS)

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Fluids play an important role in the processes of chemical and physical evolution of the crustal and mantle rocks. They intensify melting processes and polymorphic transformations, which influences on various types of deformations and re-crystallization in mineral aggregates. However the opposite processes such as catalytic effects of rocks and minerals on the chemical reactions between the fluid components, is a poorly studied topic of geochemistry related to the fluid-mineral interactions. An analysis of the catalytic transformations of fluids in the Earth's crust demonstrates a possibility for many processes being analogous to the known industry technologies, such as synthesis of hydrocarbons and their oxygen-bearing derivatives as a result of H_2O, CO, CO_2, H_2 reactions via the Fisher-Tropsch mechanism used for the production of synthetic fuel, catalytic NH_3 synthesis from H_2 and N_2 (Haber synthesis) etc. Present study is aimed to the further development of the conception about a role of the heterogeneous-catalytic mechanisms of transformations in fluids penetrating through the Earth's crust. It shows the experimental results on the catalytic activity of three crustal rocks – massive serpentinite, oceanic ophitic gabbro, and serpentine asbestos, with respect to the CH_4 vapor conversion reaction (the reaction of "synthesis-gas" formation). Serpentinite is found to be the most catalytically active rock. The degree of CH_4 conversion into H_2 increased with temperature and reached 14 vol. % at 845 °C. The methane conversion to CO and CO_2 at the same temperature was 3 vol. % for each component. An unexpected result of the experiments is a qualitative detection of CH_3OH and C_2H_5OH amongst the reaction products. Degree of CH_4 conversion into

H_2 on the asbestos was much lower than that on the serpentinite. Nevertheless, it increased with temperature from 4 % at 600-700 °C and reached 10 vol. % at 825 °C. The catalytic activity of the gabbro is minimal. The outcome of H_2 increased from 0.4 vol. % at 600 °C just to 4 vol. % at 845 °C. Degree of CH_4 conversion into H_2 on the gabbro also increased with temperature from 4-5 % at 600-700 °C and reached 9 vol. % at 845 °C. However, such experimental research can be promising in the development of hypothesis regarding the mechanisms of ozone layer degradation in the atmosphere and create some prerequisites for the formation of new scientific direction – catalytic Geochemistry. Until recently, seemingly settled view about the anthropogenic cause of ozone depletion as a result of aerosols CFCs emissions to the atmosphere due to the human activities. However, an alternative version was recently put forward, according to which the agent of ozone destruction was given to hydrogen, rising up from the depths of the Earth. In this respect, the catalytic conversion of fluids on the earth's crust rocks should be considered as a real mechanism of the additional hydrogen formation and emission from the earth's crust into the atmosphere.

PHOTOCATALYTIC GLUCOSE CONVERSION TO PRODUCE HYDROGEN IN THE PRESENCE OF TiO_2 BASED MATERIALS

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The search of alternative resources for synthesis of chemicals currently produced from non-renewable sources has directed the activities of researchers towards the use of different raw materials such as biomass [1]. Glucose, obtained from cellulose, can be used for the sustainable production of high value chemicals for instance ethanol by fermentation, sorbitol and mannitol by hydrogenation, 5-hydroxymethyl furfural by dehydrocyclization, gluconic and glucaric acids by oxidation and also to produce hydrogen [2]. Chong et al. have photocatalyticaly converted glucose to arabinose and erythrose and simultaneously obtained H_2 in the presence of Rh-TiO_2 materials [3]. The advantages of these hydrogen production approach are the use of biomass to obtain also added-value chemicals at low reaction temperature and pressure and in aqueous medium.

In the present research commercial anatase (BDH) and anatase/rutile (P25) and home prepared anatase (HPA), rutile (HPR) and brookite (HPB) TiO_2 polymorphs and have been used as supports for the deposition of metallic Pt. The Pt-TiO_2 samples have been tested in the glucose conversion under anaerobic conditions. The photoreactivity runs were carried out at room temperature in a 800 mL tightly closed N_2 saturated photoreactor irradiated in the UV region with an immersed 125 W medium pressure Hg lamp. The initial aqueous glucose concentration was 1 mM. The quantitative determination and identification of glucose and its degradation products were performed by HPLC whereas the CO_2 and H_2 evolution was followed by GC-TDC analyses.

The presence of Pt resulted essential for the production of H_2 as no hydrogen was detected by using naked TiO_2 photocatalysts. In Figure 1 are reported the concentrations of glucose, CO_2 and H_2 during the photocatalytic degradation of glucose in the presence of commercial Pt-P25 and Pt-HPR TiO_2 powders. The home prepared samples resulted more active than the commercial ones. The rutile polymorph was the most active sample both for H_2 formation and glucose conversion. The amount of H_2 formed after 420 minutes of irradiation was of 475 μmol for Pt-P25 and 1575 μmol for Pt-HPR.

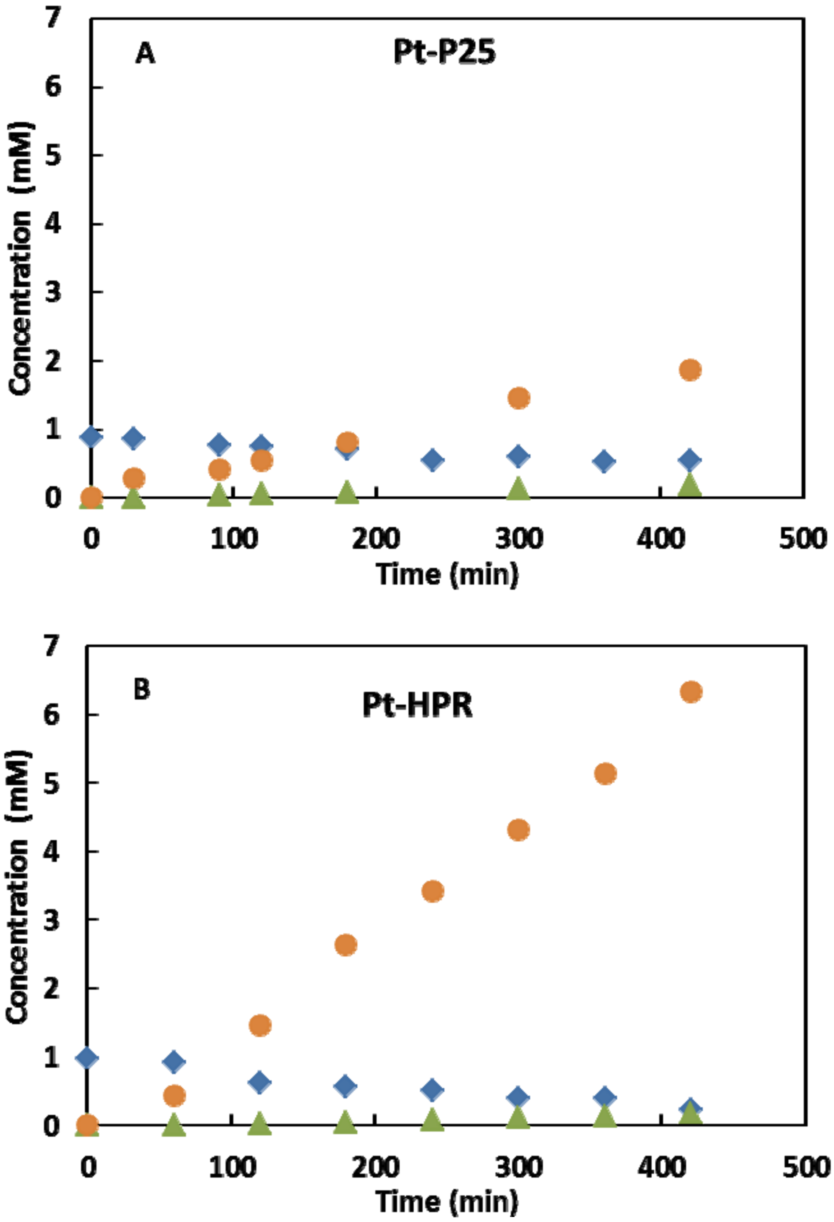

Figure 1. Evolution of concentration of glucose (◆), hydrogen (●) and carbon dioxide (▲) versus irradiation time in the presence of Pt-P25 (A) and Pt-HPR (B) samples.

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SIBERIAN SUPERCOMPUTER CENTER AS A SERVICE FOR CHEMICAL RESEARCHES

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Siberian Supercomputer Center (SSCC) [1] consists of the two high performance supercomputers which are used in shared mode by RAS institutions and universities. One of the clusters is based on massive parallel processing (MPP) architecture [2] with 576 Intel Xeon CPUs. The peak performance of this supercomputer is 30 TFlop/s. The second one is a hybrid high performance supercomputer with 80 Intel Xeon CPUs and 120 NVIDIA TESLA 2090M GPUs [3]. The peak performance of hybrid supercomputer is 85 TFlop/s. Also, SSCC has symmetric multiprocessing architecture (SMP) [4] workstation which is very popular for numerical simulation of quantum chemistry and molecular dynamics problems due to possibility of large data calculation. SMP workstation has 8 Intel Xeon CPUs with 80 cores and 1TB available RAM. Siberian Supercomputer Center use a high speed 36 TB IBRIX storage system and high speed Infiniband as an internal network.

Siberian Supercomputer Center is equipped with a lot of software which can be used for chemical researches. ANSYS CFD [5] can be used for complex chemical engineering problems [6-8]. Gaussian 09 [9] can be used fo quantum chemistry researches [10]. GROMACS [11] software package is used for molecular dynamics problems. Also, we have a lot of modern compilers for software developers which is used for ANSYS User Defined Functions or adjacent to chemical researches sciences [12], for example.

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CATALYTIC CO-HYDROPROCESSING OF WASTE VEGETABLE OILS IN THE REFINERY OF TENERIFE

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The HVOs (hydroprocessing vegetable oils) or Green Diesel, a paraffinic diesel fuel produced via catalytic hydrotreating of vegetable oils at high temperature and pressure [1], are a real alternative to fossil fuels.

In the Cepsa refinery in Tenerife several test of co-processing of waste frying oils in a gasoil hydrodesulfurization unit (HDS-I) have been done in order to study its feasibility and to investigate the possible effects of incorporating this product to the load of the unit.

This co-processing of waste oil has many advantages for the refinery, because: it needs few adaptations of existing refining infrastructure, help to reduce a hazardous waste to the environment, a biofuel with exceptional properties composed mainly for paraffins is obtained, and increase the production of gas propane in the unit gas balance, which is a sub-product very important in the energy balance of the unit.

The main element in this process is the catalyst, that offers the surface on which the reactions of hydrodesulfurization of gasoil and oil hydrotreating will take place [2]. Figure 1 shows the chemicals reactions occurring during oil hydrotreating. First, the triglycerides are hydrogenated and broken, leaving a molecule of propane and three fatty acids which continue reacting to form paraffins. [3]

The catalysts used in the reactor are CoMo / NiMo on Al_2O_3. As amply discussed in the literature [2],[3], they catalyze HDO reactions (hydrodeoxygenation) at the expense of HDC reactions (decarboxylation/decarbonylation). This favors the reduction of the formation of CO and CO_2, which temporarily, may interfere in the efficiency of HDS reactions, reducing it.

This work analyzes the co-processing of waste oil to obtain HVO at the Cepsa Refinery in Tenerife, by injecting 5-10 % of cooking oil into the load of the HDS-I unit. Some preliminary results of this process are presented as: influence of the oil injection on the properties of the gasoil and on the characteristics of the catalyst propertie, the operation of the unit and products and by-products formed.

The higher presence of the HDO reactions discussed above is illustrated in Fig. 2, where a significant increase in paraffins, following the path of HDO, can be seen.

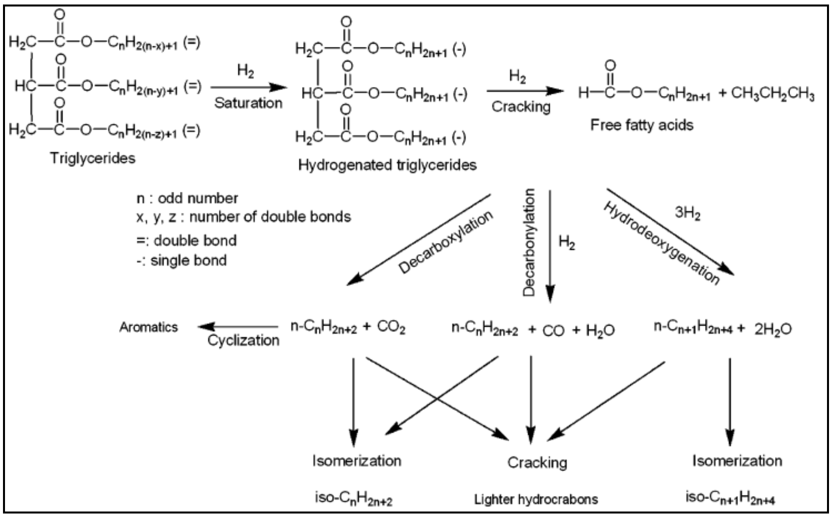

Figure 1: Possible reaction pathways of triglycerides over hydrotreating catalyst [3]

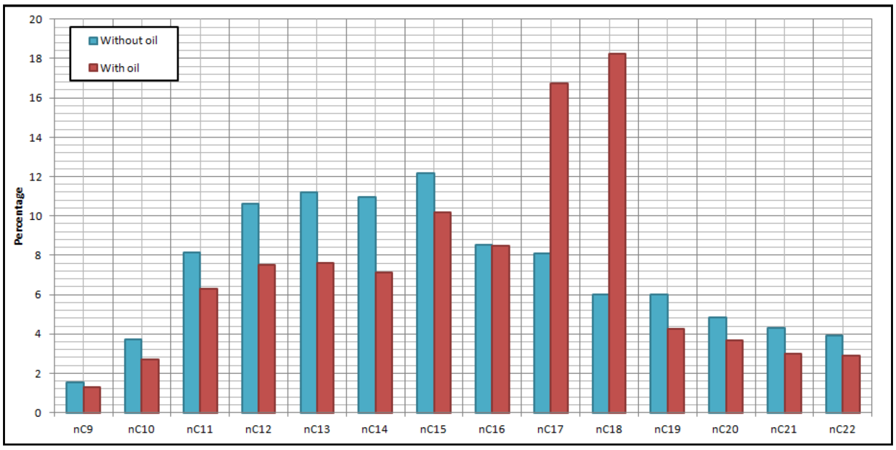

Figure 2: Analysis of the paraffins present in the Gasoil

The study shows that the main products due to oil co-processing are paraffins and propane gas. Also, during co-processing the WABT (Weighted Average Bed Temperature) increases 10 °C and improved density, cetane number of diesel and flammabitity of the final gasoil.

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INFLUENCE OF THE MAGNETIC FIELD ON CATALYTIC PROCESS OF ANAEROBIC DIGESTION OF BIOMASS

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One of the most interesting scientific problems is influence of magnetic fields on living organisms and fermentation catalysis. This influence can be caused by co-action of the constant magnetic field and field, which are created by the magnetic composites acting as the catalyst in the studied process. The magnetic composites were used as the catalyst on the basis of humic acid, which were received by method of chemical deposition in water solution of salts of two- and trivalent iron excess of ammonia, where the humic acid (HA) is present as the stabilizer.

$$2FeCl_3 + FeCl_2 + 8NH_4OH + HA \rightarrow Fe_3O_4/HA\downarrow + 8NH_4Cl + 4H_2O$$

The whole course of digestion is limited by opportunities and a condition of population of the methane-bacteria, which are extremely sensitive to temperature conditions and having small growth rate.

Horse manure was used for allocation of the methane-bacteria being used as a part of a nutrient medium of acetate. Depending on what source of carbon was used for manure fermentation, crops were done in Petri dishes dense nutrient medium of the structure stated above with acetate or methanol (DNM-1) in two weeks of fermentation of cultivations of horse manure. The dense nutrient medium containing additionally nutritious broth was also used, and 1 % of glucose (DNM-2) is as a carbon source. The Petri dishes maintained after seeding in an anaerobic culture apparatus at a temperature of 37 °C within two weeks, and then the description of the grown colonies was made. The methane-bacteria on the dense nutrient medium began to grow on the seventh days. The culture is referred to the order of 3 – *Methanococcales*, the sort *Methanosarcina* by morphological and physiological and biochemical features.

The experimental results demonstrate the ability of the growing colony-forming bacteria, as measured by the method of CFU (colony forming units) for 40 % by the addition of a magnetic composite and by 70-80 %, when the external magnetic field of 50 to 100 mT.

The presence of the catalyst and the magnetic field affects to the composition of the evolved gas (Table 1). Conditions of the analysis are presented in [1].

Table 1 – Results of the analysis of biogas, μL/μL

Process conditions	**Methane, CH_4**	**Carbon monoxide, CO**	**Carbon dioxide, CO_2**
In lack of the catalyst and a magnetic field	0,283	0,218	4,821
In the presence of the catalyst (4 %)	4,364	-	-
In the presence of the catalyst (4 %) and magnetic field (80 mT)	5,687	-	-

It is established that the speed of an exit of biogas in the presence of the catalyst (6 %) increases five times and in a magnetic field it also increases for 20-40 % at 80-100 mT.

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THE ZEOLITES FOR CONVERSION OF BIO-ETHANOL

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The steady rise in prices for petroleum feedstock in the world, which is observed in the last few years, leading to higher prices for basic petroleum products. Currently under active search for new basic raw materials that can replace oil as a fuel in the production and in the chemical industry.

One of the possible substitutes for oil, bioethanol is produced by processing biomass.

The most promising is the consideration of bioethanol as a raw material for the components of motor fuels, olefins (mainly ethylene) and aromatic hydrocarbons.

In this paper we tried to evaluate the possibility of producing ethylene and aromatic hydrocarbons from bioethanol. As the initial reactants were chosen bioethanol 1 (95 % ethyl alcohol, 5 % water) and bioethanol 2 having the following composition – ethyl alcohol (92 %) of tert-butilcarbinol (5.6 %), cyclohexane (0.64 %), acetal (0.61 %), isopropyl alcohol (0.47 %), toluene (0.39 %). As catalysts of the process have been studied zeolites – 3A, 4A, 5A and 13 X. The experiments on the influence of the nature of the carrier on the of the products yield have been studied as a flow of inert gas and without it. The conversion of bioethanol 1 in a stream of inert gas over the 3A zeolite produces about 12 vol. % hydrogen and small amount of carbon monoxide and ethylene. The same results are typical of other zeolites. At the conversion of ethanol without adding an inert gas into the reaction mixture increases the yield of products. Over the zeolite 3A is formed synthesis gas with a ratio of H_2: CO = 1: 1.2 and ethylene with a concentration of 18.3 vol. %. Zeolite 4A runs in the direction of the formation of hydrogen, wherein the hydrogen concentration in the reaction product reaches a value of 33 vol. %. The highest yield of ethylene (54 vol. %) is formed over the 5A zeolite. Over the 13 X zeolite a substantial amount of carbon monoxide (36 vol. %) is formed, also in the reaction products are observed of H_2 (5.4 vol. %) and ethylene (18.6 vol. %). It should be noted that at conversion of

95 % ethyl alcohol over these zeolites liquid hydrocarbons are not formed. Then, when used an bioethanol 2 as feedstock special changes in the composition of gaseous products is not observed. Also active on the yield of ethylene is carrier 5A, the ethylene concentration in the reaction products up to 42 vol. %. Over the 4A carrier is formed the synthesis gas with a ratio of H_2: CO = 1.5: 1, wherein the hydrogen concentration is 28 vol. % and CO – 18 vol. %. In the conversion of bioethanol 2 over the zeolite 3A liquid reaction products contain toluene. In the study of the conversion of alcohol in the inert gas flow is formed about 20 vol. % toluene, conducting the reaction without addition of argon to the reaction mixture leads to increase of the concentration of toluene to 24 vol. %. Besides toluene liquid reaction products formed in trace amounts of benzene. About 5 vol. % of toluene formed over the zeolite 4A. Over the other zeolites (5A and 13X), liquid hydrocarbons are not formed.

According to the results it can be assumed that over the investigated zeolites several reactions have places as dehydration reaction, cracking, reforming of ethanol, and ethylene oligomerization (Figure 1).

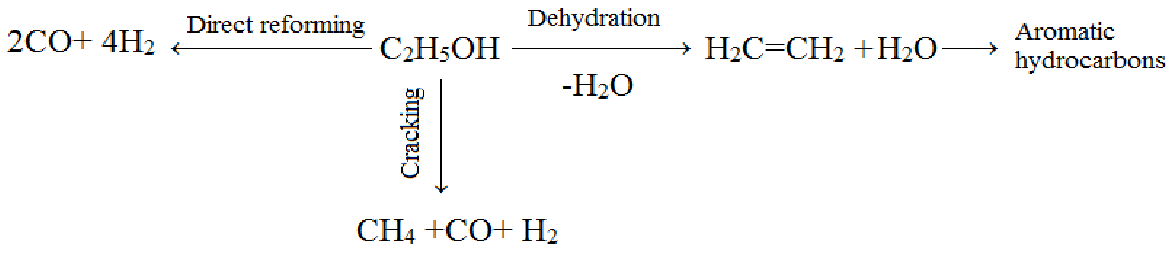

Figure 1. The scheme of ethanol conversion over zeolites

Thus the study of conversion of industrial alcohol and ethyl alcohol over zeolites allows to identify the products of dehydratation of alcohol – ethylene, cracking – methane, reforming – hydrogen and carbon monoxide. Also aromatic hydrocarbons – toluene, benzene, which are the next products of ethylene oligomerization. Formation of toluene at conversion of industrial alcohol may also depends on the presence of additives tert-butilcarbinol, cyclohexane, and others in the composition of alcohol. The explanation of this will be the subject of our following research works.

LIGNIN VALORIZATION FROM KRAFT BLACK LIQUOR BY ITS DEPOLYMERIZATION

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Lignin is the second most plentiful polymer in the nature after cellulose. It is considered as an amorphous biopolymer composed by combination of three phenylpropane monomers: coniferyl, sinapyl, and p-coumarylalcohol. These monomers are connected by ether and carbon-carbon bonds, forming a randomized structure in a three-dimensional network [1].

Around 70 million tons of lignin are produced worldwide, but only about 2 % is commerciallized for its utilization as a chemical product [2]. The main process where lignin is produced is the Kraft pulping, with approximately 90 % of the world chemical pulp production. The black liquor is the main byproduct of this process, which contains tipically 30-35 % of lignin in dry solid weight basis [3]. This stream is traditionally concentrated in evaporators and then burned for energy generation and chemicals recovery. However, the energy generated by burning the black liquor is greater than the process demand and besides that, this stage is the “bottleneck” of the pulping process [4]. Hence, the valorization of lignin as chemical precursor can be an option of sorting out this problem and obtaining and extra revenue in the process.

Different options have been evaluated for the lignin valorization, such as pyrolysis or gasification; however, they are energetically expensive procedures. On the other hand, the adquisition of phenolic monomers could be achieved by means of thermochemical treatments that require less harsh conditions to depolymerize lignin to low-molecular weight compounds.

In the present work, *Eucalyptus globulus* Kraft black liquor from “Papelera Guipuzcoana de Zicuñaga” (Spain) was used for the lignin depolymerization. In the first place, a characterization stage was conducted, raising the high dry content of the liquor (14.00 ± 0.45 %) and the lignin content (67.4 ± 5.41 g/L), which demonstrates the high lignin content of this stream.

The depolymerization stage was carried out according to the process described by Erdocia et al. [6] at 300 °C and 80 min, achieving a pressure of 9 MPa. Three main groups of products were produced during the reaction: oil, enriched in phenolic monomers; residual lignin, resulted from the repolymerization reactions and a solid product formed by char.

A comparison study of the lignin conversion into phenolic compounds was carried out using different agents (a capping and an oxydant) to increase the phenolic products yield and reduce the char formation. Phenol and hydrogen peroxide were used with this purpose in homogeneous phase reaction with a lignin:facilitating agent ratio of 1:0.5 (% wt.). Also a blank depolymerization was perfomed.

The highest yield regarding the oil production was obtained by the reaction with phenol as capping agent, with around 30 % of conversion from the original lignin. However, the minimum yields for undesired products were obtained with hydrogen peroxide as oxydant agent for the residual lignin (32 % w/w) and without any facilitating agent for the coke formation (less than 15 % w/w).

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PP-10

ENHANCED CATALYTIC PERFORMANCE OF Pd/SiC FOR HYDROGENATION OF FURAN DERIVATIVES AT AMBIENT TEMPERATURE UNDER VISIBLE LIGHT IRRADIATION

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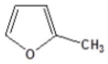
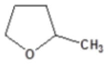
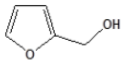
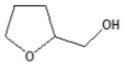
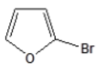
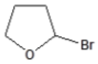
Recently, photocatalytical selective transformations of organics are becoming increasingly noticeable [1,2]. Metal oxide semiconductors and plasmonic metals are widely employed as photocatalysts to catalyze the oxidation of alcohols and amines, C-H bond activation and reduction of nitroaromatics [3,4]. Palladium (Pd) is widely used as catalysts in heterogeneous catalytic reactions [5]. Cubic SiC (β-SiC) is a non-oxide semiconductor with a band gap of ~ 2.4 eV [6,7], which enables it absorb visible light, therefore it can produce energetic photo-generated electrons under light irradiation. If the energetic electrons can efficiently transfer to Pd nanoparticles supported on SiC by means of Mott-Schottky contact, the intrinsic catalytic activity of Pd for furan hydrogenation is expected to be enhanced significantly.

Table 1. Photocatalytic hydrogenation of furan derivatives over Pd/SiC catalyst[a].

Reactant	Main product	Conv.(%)	Select.(%)	TOF(h^{-1})
		99	99	70
		99	99	70
		99	99	70
		95	81[b]	56
		89	78[b]	49
		81	70[b]	40

[a] Reaction conditions: 4 mmol reactant, 80 mg 3 wt % Pd/SiC catalyst in n-amyl alcohol (10 ml) at 25 °C and 1 MPa of H_2, reaction time 2.5 h, and irradiation intensity 0.15 W/cm^2. [b] The other products are alcohols, acids and esters due to the ring hydrogenolysis of furan derivatives.

Powder-like β-SiC support with a specific surface area of 48 m^2/g was prepared by a sol-gel and carbothermal reduction route, and the 3 wt % Pd/SiC catalyst was prepared via a liquid phase reduction method. β-SiC has strong UV and visible absorption. The maximal peak appears at about 375 nm. However, the Pd/SiC catalyst displays stronger absorption in UV and visible range, indicating that the light energy can be better exploited by the catalyst. The photocatalytic performances of 3 wt % Pd/SiC catalyst were conducted in an n-amyl alcohol solution under the irradiation of a 300 W Xe lamp (400-800 nm). Over the Pd/SiC photocatalyst, the yield of tetrahydrofuran (THF) from furan hydrogenation is 99% and the turnover frequency (TOF) is 70 h^{-1} at 25 °C and 1 MPa of H_2 (Table 1, entry 1). These are comparable to the thermal catalytic results (The yield and TOF are 98 % and 16 h^{-1}, respectively, at 40 °C and 8 MPa H_2) [8]. Control experiment reveals that the Pd/SiC catalyst in dark can only achieve a furan conversion of 37 %, suggesting that the high activity of the Pd/SiC under irradiation mainly results from the light driving. Moreover, the catalyst has the general applicability for these reactions (Table 1, etries 2-6). Under the same temperature and pressure condition, increasing of the light intensity resulted in a nearly linear increase for the conversion of furan. Because the Pd/SiC catalyst has strong absorption to the light with wavelengths below 460 nm, the light in the 400-450 nm wavelength range contributions the highest light-induced conversion (35 %). While the irradiation in the wavelength ranges of 450-530 and 530-600 contributes 29 % and 23 % to the conversion, respectively.The heterojunction between SiC and Pd can facilitate the quick transfer of photogenerated electrons from SiC to Pd. These energetic electrons on the surface of Pd nanoparticles significantly enhance their intrinsic catalytic activity. The novel processes using Pd/SiC photocatalyst have potential to utilize solar energy and are greener than conventional catalytic processes driven by heating.

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INTERESTERIFICATION OF VEGETABLE OILS WITH METHYL ACETATE IN THE PRESENCE OF HETEROGENEOUS CATALYSTS

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Biodiesel is obtained from triglycerides via transesterification based reactions [1]. The produced biofuel has different advantages with respect to petroleum derived diesel, such as sustainability, biodegradability, non-toxicity, lower harmful emissions, higher flash point, excellent lubricity and superior cetane number [2].

In principle, biodiesel has a huge potential as an alternative fuel, but it is estimated that the cost of biodiesel is still about two times higher than that of the petroleum based diesel fuel [3]. Obtaining crude oil from microalgae and the development of catalysts for this green biomass conversion technology may significantly decrease the production costs of biodiesel.

Chemical interesterification is an important technological option for the production of biodiesel. In the interesterification an ester is used as acyl donor to produce fatty acid alkyl esters [4]. The interesterification of oils and fats with methyl acetate provides a promising alternative to transesterification because of the formation of triacetin as co-product, instead of glycerol. In fact, while glycerol must be separated from the product mixture and has already a saturated market [5], triacetin is miscible with the esters and may contribute to the formulation of biodiesel (up to 10 wt %), still keeping the requested quality standards of the fuel [6]. In addition, in the interesterification process reagents are perfectly miscible, thus interfacial mass transfer resistances, typical of the transesterification of triglycerides with low molecular weight alcohols, vanish.

Heterogeneous catalysis could improve the performances of the interesterification process while allowing easy catalyst separation and recovery from reaction mixture. In this work we studied tin based heterogeneous catalysts for the interesterification of rapeseed oil using methyl acetate as acyl donor. The experiments were performed in batch reactor by varying different operating parameters, such as alkyl acetate / oil ratio, reaction time, temperature and catalyst concentration. A wide range of temperature was investigated (150-240 °C), which allowed to identify a threshold value below which the reaction does not take place. Interesting results were obtained with tin oxide- catalyst: for example, yields higher than 90 % were achieved after 4 hours of treatment at temperatures of 210 °C and a molar ratio methyl acetate / oil equal to 40. Tests at different treatment time (0.25-4 h) were performed to study the kinetics of the process. Also the possibility of reuse the catalyst for different reaction batches was investigated with satisfactory results.

A more detailed description of collected results will be presented during the conference.

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THE EFFECT OF WATER-IMMISCIBLE LIQUID ORGANIC PHASES ON THE RATE OF BIOCATALYTIC METHANE OXIDATION

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Methane can be produced by methanogenic bacteria from biomass and thus it is a renewable source for various chemicals production. For example methanotrophic bacteria during biocatalytic methane oxidation can produce valuable chemical products such as single cell protein, amino acids, enzymes, lipids, vitamins (B_6 and B_{12}) and polysaccharides [1]. For effective use of biocatalytic methane oxidation it is important to study kinetics and develop ways for intensification of the process. The aim of this study is kinetic modeling of biocatalytic methane oxidation and exploring the possibility of intensification of this process by introducing of water-immiscible organic liquid phases (WILOPs) into the reaction aqueous medium. It was shown that methane biooxidation rate depends simultaneously on the concentrations of methane and oxygen in the reaction medium. This suggests that in order to describe the methane oxidation process multisubstrate kinetic equations can be used:

1) multiplicative kinetic equations [2]

$$r = r_1(c_1) \cdot r_2(c_2) \quad , \tag{1}$$

where r – methane oxidation rate; c_1, c_2 – concentrations of methane and oxygen respectively; $r_1(c_1), r_2(c_2)$ – individual kinetic equations for methane and oxygen respectively. As an individual kinetic equations for methane and oxygen were considered as follows: Monod's equation, Moser's equation, Tissier's equation [2].

2) kinetic equation of ternary complex mechanism [3]

$$r = \frac{r_{\max}}{1 + K_2/c_2 + K_1 K_2/c_1 c_2}\,, \tag{2}$$

where $r_{\max}$ – maximal specific rate of methane oxidation; K_1, K_2 - constants for oxygen and methane respectively;

3) kinetic equation of "ping-pong" mechanism [3]

$$r = \frac{r_{\max}}{1 + K_1/c_1 + K_2/c_2}\,. \tag{3}$$

Parameters of these kinetic equations were determined using nonlinear regression analysis. Adequacy of the kinetic equations was evaluated by multiple correlation coefficient (R). The results of calculations demonstrated that for the most accurate prediction of the process rate Moser-Moser kinetic equation must be used (R = 0,951). On the basis of Moser-Moser equation macrokinetic model of biocatalytic methane oxidation was developed. This model takes into account kinetics of methane oxidation by bacteria and mass transfer of methane and oxygen from gas phase to liquid aqueous medium. Using this model it was shown that the process can be intensified by increasing the mass transfer rate of poorly soluble gases (O_2 and CH_4) to the aqueous phase. One of the possible ways of gas-liquid mass transfer intensification is introducing of WILOPs into the reaction medium. The effect of WILOPs (*n*-dodecane, perfluoro-N-(4-methylcyclohexyl)piperidine (PMCP) and polydimethylsiloxane (PDMS)) on the rate of biocatalytic methane oxidation was studied (table).

Table. The effect of WILOPs on the rate of biocatalytic methane oxidation

WILOPs	r, mmol/(l·h)	r/r_0	$K_La/K_{L0}a_0$
n-Dodecane	3,0±0,1	1,30	5,6
PMCP	2,8±0,2	1,22	3,7
PDMS	2,7±0,1	1,17	3,0
Aqueous medium without WILOP	2,3±0,1	1,00	1,00

Note: r and r_0 are the rates of methane oxidation in the presence and absence of WILOPs respectively; K_La and $K_{L0}a_0$ are volumetric mass transfer coefficients of oxygen in the presence and absence of WILOPs respectively.

It was shown that increasing of methane oxidation rate in the presence of various WILOPs was not identical (Table). It can be explained by different effects of WILOPs on gas-liquid mass transfer intensity.

The data obtained can be used for the development of methods for intensification of biocatalytic methane oxidation.

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NATURAL HALLOYSITE NANOTUBES AS COCATALYSTS IN THE HYDROTREATING PROCESS OF MIXTURE OF STRAIGHT-RUN DIESEL FRACTION WITH COTTONSEED OIL

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Elaboration of processes for producing motor fuels involving plant resources in the structure of the modern oil refinery is the next step in the development of the market of alternative motor fuels. One of such processes is a process of co-hydrotreatment of diesel fractions in addition to their composition 5-10 % of vegetable oils in the temperature range of 300-350 °C and a hydrogen pressure of 3,0-3,5 MPa. Typically in this process as a catalyst can be used a conventional hydrotreating catalysts and also their modifications. The main problem with conventional hydrotreating catalysts is that released in the hydrotreating of vegetable oils water destroys the catalysts and reduces their lifespan.

In the present study the process of co-hydrotreating of diesel fraction with a content therein of 10 % of cottonseed oil with using as a catalyst natural halloysite nanotube in a mixture with a Ni, Mo containing catalyst of hydrotreating AGKD-400 BN was investigated.

Halloysites are kaolinite clay minerals with a high ratio of Al/Si in comparison with other aluminosilicates. They have a hollow tubular structure in a range submicron and consist of aluminum and silicon oxide layers. Halloysite nanotube have a high specific surface area (80-150 m^2/g), therefore, have a high cation exchange capacity in the range of 0,02-0,68 mol/kg. Halloysite nanotubes in hydrated state can adsorb low molecular weight substances in the interlayer space, however a high-molecular substances (molecular weight above 300 g/mol), in the inner lumen of halloysite tube.

Material balance of straight-run diesel fraction’s hydrotreating with the content in it 10 % cottonseed oil with the addition of natural halloysite nanotubes to the catalyst AGKD BN-400 is shown below.

PP-13

	AQKD-400	AQKD-400/halloysite
Is taken, % wt.: straight-run diesel fraction	88,3	87,8
cottonseed oil	8,9	8,8
hydrogen	2,8	2,6
Obtained % wt.: Diesel fraction of 180-350 °C	93,3	93,3
Gasoline fraction NK-180 °C	1,5	1,8
C_1-C_4 gases	2,3	2,6
water	0,8	0,6
coke	0,8	0,6
losses	1,3	1,1

As seen from the above data, the addition of halloysite to main hydrotreating catalyst reduces the hydrogen consumption by 7.14 % (wt), due to the fact that there is a shift of the deoxygenation reaction towards the reaction of decarboxylation and dekarbonylation. Addition of the halloysite to the base composition of catalyst can lead to a reduction by 25 % of coke and of water which is produced during the process, and this favorably affects the lifespan of the main hydrotreating catalyst.

CATALYTIC PROCESSES OF PRODUCTION OF EPOXIDES AND CARBOXYLIC ACIDS FROM RENEWED RAW MATERIALS

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Processing of natural renewable raw materials makes it possible to produce industrially claimed materials, such as epoxides, mono and dicarboxylic acids. These materials have found a wide application in different fields. The carboxylic acids, involving along with carboxylic groups some other functional groups, can be used as matrixes and building blocks for synthesis of medical preparations or their precursors.

The method of phase-transfer catalysis with bifunctional homogeneous catalysts based on the peroxopolyoxotungstates $Q_3\{PO_4[WO(O_2)_2]_4\}$ is a very promising way to perform oxidation transformations of natural raw materials into novel biologically active materials [1]. A simultaneous application of phase-transfer catalysts as quaternary ammonium cations (Q^+) and oxidation catalysts as peroxopolyoxotungstates permits one to perform oxidation processes by H_2O_2 during one technological step.

In the present work we have screened different substrates such as cycloolefins, unsaturated fatty acids and their ethers, lupane-type triterpenoids, coumarins and amines. The oxidation reaction was performed in a two-phase system. Most of the resulting products – derivatives of betuline, peucedanine, unsaturated fatty acids and amines – exhibit antiviral, antiinflammatory and anticancer action [2, 3].

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PP-15

THE CATALYSIS OF NANOSCALE MAGNETIC COMPOSITES ON THE BASIS OF HUMIC ACIDS OF ANAEROBIC DIGESTION OF BIOMASS

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The presence in the molecules of humic acids (HA) variety of fragments and functional groups that makes them potential participants in a very wide range of interactions. For example: complexation with metals, interactions, hydrophobic interactions, formation of complexes with charge transfer, redox-activity, interaction through hydrogen bond and the van der Waals forces, adsorption on mineral surfaces, the influence on the interfacial distribution of substances.

Humic acid is a natural redox polymers, i.e. polymers having electronic conductivity due to the presence in the circuit close to each other groups that can reversibly be oxidized and recover. The redox activity of humic acids plays a crucial role in the emergence and development of redox processes in soils, peats, coals.

These properties of humic acid in our opinion determine the properties of humic acids, as a basis to create a catalyst of methane digestion of biomass.

Magnetic composites based on humic acids were obtained by chemical co-precipitation in an aqueous solution of salts of ferrous and ferric iron excess alkali in the presence of, as a stabilizer, humic acid:

$$2FeCl_3 + FeCl_2 + 8NH_4OH + HA \rightarrow Fe_3O_4/HA\downarrow + 8NH_4Cl + 4H_2O$$

Study of transmission electron microscopy of nanocomposites showed that there is a homogeneous distribution of nanoparticles in the structure of the macromolecular matrix. It is revealed that the Fe_3O_4 nanoparticles are spherical particles with a diameter of 7-10 nm. The humic acid macromolecule binds particles immediately after the nucleation of Fe_3O_4 nanocomposite, preventing their further growth. The IR-spectra of the nanocomposite have intensive bands in the area 1530-1570 cm^{-1} (C=O), 1360-1370 cm^{-1} (C=O), 400-600 cm^{-1} (Fe–O), 3400-3000 cm^{-1} (O–H).

The analysis of Mössbauer spectra of nanoparticles has allowed establishing that the particles of the investigated nanocomposites demonstrate super-magnetic behavior. The core of the nanocomposite is a mixture of non-stoichiometric magnetite and maghemite. With increasing humic acid content in the nanocomposite precursors increases the relative content of the new phase formed on the surface of the particles resulting from the interaction of iron oxides and humic acid. The parameters of the partial spectrum of ^{57}Fe nuclei in the structure of the new phase correspond to the atoms of Fe^{3+} in octahedral environment of oxygen atoms. The particle size is reduced: d (20 % HA) = 13.5 ± 0.1 nm, d (50 % HA) = 12.3 ± 0.1 nm. Some magnetic properties of the obtained Fe_3O_4–HA nanocomposite (*in situ*): the maximum magnetization – 6.81 emu/g, the remanence – 1.1 emu/g, the coercive force – 89 Oe, the Squareness of the hysteresis loop – 0.16.

In the example of horse manure it is shown that methane fermentation is divided into two phases: acid and alkaline (gasification). Both phases are carried out simultaneously and in parallel in a single volume.

Degradation products of organic matter produced in the first phase are substrates for microorganisms of the second phase. The composition of the intermediate products formed during anaerobic digestion, depends on the composition of the biomass. At the beginning of the process, when the amount of substrate exceeds the number of micro-organisms, their accumulation during the fermentation process determines the rate of methane formation. At the end of the experience speed drops due to the depletion of raw materials.

The results show that the process time and the degree of conversion of biomass depend on the pH of the medium, the temperature of the process. Optimum conditions are pH = 7.0 and temperature – 40 °C. The process is reduced more than five times at a pressure of magnetic composite to 6 %, and accelerated as the stage of the formation of microorganisms and methane formation. Under optimal conditions, the methane formation is carried out without an incubation period. The results of chromatographic analysis indicate that in the absence of catalyst in the gas phase contains, along with CH_4, the monoxide and carbon dioxide, while in the presence of a magnetic composite methane is the only product of the gas phase.

PP-16

CATALYTIC CONVERSION OF SYRINGOL, CATECHOL AND 4-METHYLCATECHOL OVER ZSM-5 ZEOLITE

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Fast pyrolysis in the presence of a catalyst is a process that is being considered for the upgrading of the biomass pyrolysis vapors in order to produce a bio-oil with improved properties. However, the pyrolysis vapors are an extremely complex mixture of oxygenated compounds and due to this complexity, there is limited knowledge of the reaction mechanisms that take place during catalytic upgrading. A better understanding of the reaction mechanisms can be gained through the pyrolysis of individual model compounds that can be found in biomass pyrolysis vapors. In literature, several groups have studied the pyrolysis of model compounds, either thermally to investigate the mechanisms of secondary cracking reactions, or catalytically to investigate the catalytic conversion mechanisms. The most common catalyst used is the ZSM-5 zeolite, which is also the most frequently studied catalyst for the catalytic pyrolysis of biomass.

In this work, fast pyrolysis vapors of syringol, catechol and 4-methylcatechol (characteristic products of lignin pyrolysis), obtained at 400-600 °C, were catalytically converted over a ZSM-5 zeolite catalyst in a fixed bed reactor. Experiments with a non-catalytic material (silica sand) were also conducted in order to identify the differences between catalytic and thermal reactions. In our preliminary results, catechol and 4-methyl-catechol were found to be very stable thermally, as no significant conversion was observed until the temperature was raised to 600 °C. Syringol decomposed more readily at 500 °C, while its full conversion was observed at 600 °C. The products from the catalytic conversion of catechol and 4-methylcatechol were phenols and catechols (with or without methyl substitutes), while at 600 °C aromatic hydrocarbons and napthalenes were also observed. The catalytic conversion of syringol yielded a wider array of compounds, such as substituted phenols, catechols, guaiacols, benzofurans, aromatic hydrocarbons and napthalenes.

Acknowledgements

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PP-17

PRODUCTION OF GREEN DIESEL BY HYDROTREATMENT OF JATROPHA FATTY ACID METHYL ESTERS OVER γ-Al_2O_3 AND SiO_2 SUPPORTED NiCo BIMETALLIC CATALYSTS

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γ-Al_2O_3 and SiO_2 supported NiCo bimetallic catalysts were synthesized for the production of diesel fuel by the hydrotreatment of jatropha fatty acid methyl esters. Both the NiCo/γ-Al_2O_3 and NiCo/SiO_2 catalysts were synthesized by co-impregnation method and were characterized by X-ray Diffraction analysis, Fourier Transform Infra-Red Spectroscopy, Temperature Programmed Reduction and Brunauer–Emmett–Teller and Barrett–Joyner–Halenda methods. A maximum conversion of 78.27 % and 76.12 % were obtained for NiCo/γAl_2O_3 and NiCo/SiO_2 respectively under the reaction conditions of 2 MPa and 400 °C and straight chain alkanes in the diesel range (C12-C20) were the main products. Influences of reaction time and reaction temperature on the conversion and product selectivities were studied.

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CARBON NET FROM NANOSPHERES AS EFFICIENT METAL-FREE ELECTROCATALYSTS FOR OXYGEN REDUCTION REACTION

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The oxygen reduction reaction (ORR) one of the two half-reactions in fuel cells is one of the bottlenecks that has prevented fuel cells from finding a wide range of applications today. This is because ORR is inherently a sluggish reaction; it is also because inexpensive and sustainable ORR electrocatalysts that are not only efficient but also are based on earth-abundant elements are hard to come by. Herein we report the synthesis of novel carbon net composed of nanospheres materials that can contribute to solving these challenges associated with ORR. Mesoporous oxygen-doped carbons were synthesized from in situ polymerized glucose by carbonization in Ar atmosphere of the latter. The metal-free, glucose-derived mesoporous carbon net exhibited the excellent activity, superior to 10 wt % Pt/C commercial catalyst. This unprecedented activity by the metal-free carbon net toward ORR was attributed to the synergetic activities of unique nanostructure and oxygen (or hydroxyl) species in it during pyrolysis.

PP-19

PHENOL HYDRODEOXYGENATION OVER A Pt/γ-Al_2O_3 CATALYST

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Cellulosic biomass can be converted into transportation fuels bythree major pathways: syngas production by gasification, bio-oilsproduction by pyrolysis or liquefaction, and aqueous sugar byhydrolysis. Bio-oilfrom is considered as an alternativeto petroleum-based sources for a wide range of fuels and high value-added chemicals and other products. The major organic compounds of the bio-oils are acids, alcohol, ether, ketone, aldehyde, phenol, ester,sugar, furan, and nitrogen compounds. The phenolics compositions (phenol, guaiacol and other substituted phenol compositions) are formed by decomposition of lignin. Phenols have been receivedconsiderable attentions because of their low reactivity in HDO process. The main objective of this work is the kinetic study of the liquid-phase catalytic hydrodeoxygenation of phenol which is a representative model compound of bio-oil. The experiments were conducted over a Pt/γ-Al_2O_3 catalyst in crushed form, in order to eliminate the internal diffusion phenomena.

The experiments were conducted in a mini scale spiral string bed reactor with internal diameter 2.1 mm. The reactor was loaded with 0.25 gr of catalyst. The liquid feed consisted of 1 % phenol diluted in n-hexane. The solvent was selected to ensure low volatility and enables the study of phenol hydrogenation in liquid phase in the range of the conditions tested.Two liquid feed rates were tested corresponding to WHSVs 21 and 32 h^{-1}.The experiments were performed at pressure 30 bar, and temperatures within the range 40-170 °C. The H_2 feed rates were high enough to ensure restriction of the external mass transfer effects from the gas to solid phase, and correspond to gas to liquid feed ratio G/L=445±10 Nl/l. Standard experiments were repeated at regular time intervals for the determination of the catalyst deactivation. The analysis of the samples was conducted by gas chromatography. The detected substances were phenol, cyclohexanol, cyclohexane and cyclohexene (traces). Pt/γ-Al_2O_3 catalyst was very active for the HDO of phenol even at low temperatures. Cyclohexane selectivity increases with temperature increase above 150 °C. However, cyclohexanol selectivity was 99-95 % at temperatures between 40 and 150 °C.

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THE CATALYST OF WOOD DELIGNIFICATION: A NEW ROUTE FOR THE SYNTHESIS OF ANTHRAQUINONE

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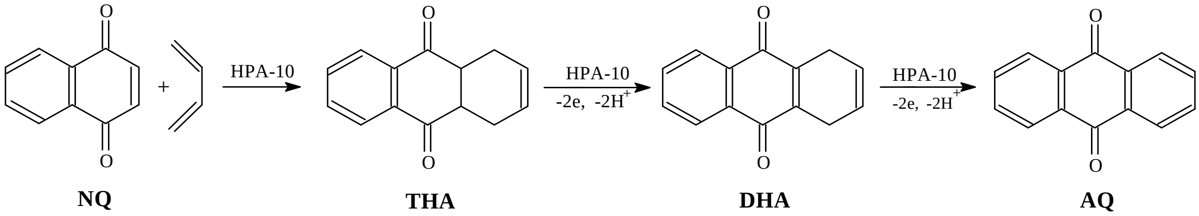
Currently 9,10-anthraquinone (AQ) and its derivatives are used as catalysts in processes of delignification of wood. A growing demand for AQ and its derivatives cannot be provided with archaic technologies of their manufacture. So, acylation of benzene by phthalic anhydride according the Friedel-Krafts reaction followed by cyclization of *ortho*-benzoylbenzoic acid is the main industrial method of AQ preparation. However, in this process there is a problem of utilization of excessive acid catalyst. In another industrial process based on 1,3-butadiene reaction with 1,4-naphthoquinone (NQ), concentrated alkalies, and strong inorganic oxidants are used [1]. The two industrial processes produce a lot of wastes. Thus there is a problem of creating a new environmentally friendly process of AQ production.

For this purpose heteropoly acids can be used. Now processes using aqueous solutions of Mo-V-P heteropoly acids with Keggin composition $H_{3+x}PV^{V}_{x}Mo_{12-x}O_{40}$ (HPA-x) are widespread [2]. Unlike many other oxidizing agents, V(V)-containing HPA-x solutions are able to be regenerated by O_2. Thus they can catalyze the oxidation of various substrates by O_2. In the presence of HPA-x solutions these processes consist of 2 stages carried out in separate reactors **1** and **2**. In the first stage a substrate is oxidized by HPA-x. In the second stage HPA-x is regenerated by O_2. Thus HPA-x solutions may be considered as *reversible oxidants*. Furthermore, the HPA-x solutions are strong Brønsted acids and can be used as acid catalysts. Therefore, these solutions can be *bifunctional* (i.e. oxidative and acidic) catalysts.

We have developed a new process of AQ production in the presence of HPA-x solutions [3, 4]. At that, we have combined *in a single technological stage* 2 types of reactions: 1) the acidic-catalyzed Diels-Alder reaction of 1,3-butadiene with NQ giving 1,4,4a,9a-tetrahydro-9,10-anthraquinone (THA); 2) oxidation of THA by HPA-x with the formation of 1,4-dihydro-9,10-anthtaquinone (DHA) and then AQ. Thus, our *one-pot* process is described by scheme 1. In [3], this process was carried out in the absence of an organic solvent, but a mixture of products was obtained (49 % AQ). In

[4], where we have used water-miscible organic solvents, the yield of AQ has increased.



Scheme 1. Preparation of AQ in the presence of HPA-10 solution

In this process which proceeds in the reactor **1** at 80 °C in the presence of water-miscible organic solvents (acetone, 1,4-dioxane), the solution $H_{17}P_3Mo_{16}V_{10}O_{89}$ (HPA-10) is used. The formed AQ is practically quantitatively (96 %) precipitated and is separated by filtration from the reduced catalyst. Yield of AQ is 70 %, content of AQ in the product obtained under these conditions reaches 97 %. The organic solvent may be separated from the filtrate by distillation and is used again.

Further the reduced HPA-10 solution (after separation of the organic solvent) is oxidized by air O_2 in the reactor **2** ($t > 100$ °C, $P_{O_2} = 2$-4 atm). In so doing, a direct contact between 1,3-butadiene and O_2 is excluded.

Our total process *is waste-free* owing to ability of the HPA-x solutions to be regenerated. Studies in Siberian Scientific-Research Institute of Wood and Pull-and-Paper Industry (Bratsk, Russia) have shown that the formed AQ may be used as the *effective catalyst* for wood delignification. Our product is fully comparable with usual commercial AQ obtained via the many-stage technology.

Our technology of production of the delignification catalyst (AQ) has become more effective after we had developed a new method of synthesis of high vanadium non-Keggin HPA solutions which are stable at elevated temperatures (160-170 °C) and have a high oxidative potential. This feature of the HPA-10 solution has ensured high yield of pure AQ in the process depicted in the Scheme 1.

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PP-21

BIFUNCTIONAL Pd(Pt)/ZrO_2 CATALYST FOR EFFECTIVE ONE-POT PROCESS OF ALKANES PRODUCTION FROM CARBOXYLIC ACIDS

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Nowadays investigation related to green chemistry is of great importance in catalytic organic synthesis. Production of the effective catalysts for highly-selective synthesis of valuable organic compounds from the products of renewable materials transformation is a top priority task for leading research centers of the world. Utilization of bio-derived carboxylic acids is one of the direction of investigation in heterogeneous catalysis [1, 2]. Decarboxylation, etherification of fatty acids, hydrogenation and isomerisation of aliphatic fatty acids, conversion of hydroxyacids into glycols, etc. require the development of new catalytic routes as well as active and selective catalysts. Carboxylic acid ketonization followed by hydrogenation of obtained ketone into alkanes over bifunctional catalysts is a promising alternative method to synthesize fuel components [2].

The aim of this work was to find effective catalyst for selective valeric acid conversion into n-nonane over single bed bifunctional catalyst. For this the influence of reaction parameters such as temperature, hydrogen pressure, gas atmosphere, as well as metal dispersion on catalytic behaviour in valeric acid ketonization and 5-nonanone hydrogenation, i.e. stages of one-pot process, were investigated. The ketonization and hydrogenation were studied in presence of ZrO_2, CeO_2, Al_2O_3, MnO_2, TiO_2 oxides and Pd(Pt) catalysts supported on ZrO_2 and CeO_2, respectively. The used catalysts were characterized by different physicochemical methods (BET, XRD, XPS, IR and UV-vis spectroscopy). The kinetics of these processes was studied. The correlation between catalytic behaviour and properties was established. Based on the obtained results, the active and stable catalyst was found for one-pot valeric acid conversion into n-nonane. In addition, one-pot process was shown to be more effective compared with two-step process.

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PP-22

HIGH-TEMPERATURE PROCESSING OF SEWAGE SLUDGE

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Currently, the wastewater treatment sludge at aeration stations is used as fertilizer.

However, this material can serve as the raw for many types of industrial production. The sludge isolated at treatment of the sewage of cities and localities with a small fraction of untreated industrial effluents is a valuable organo-mineral mixture by chemical composition. Analysis of the sludge residue composition and the dynamics of origin of the components of this mixture allows us to consider it as a potential organic raw.

In this regard, it is useful to test its conversion in the conventional processes of treatment of such hydrocarbons that have arisen from the same biological precursors that the sludge components.

In this paper we study pyrolysis, i.e. the processing of carbonaceous materials by high-temperature heating without air in several regimes: fast and slow pyrolysis to produce a polycarbone (char), a liquid hydrocarbon mixture, and pyrogenetic water, fuel gas.

Tests were carried out on an apparatus consisting of a metal reactor with tapping the gaseous products at the top and the liquid products at the bottom, equipped with a condenser.

The technology of fast pyrolysis of sludge was applied up to 800 °C with a heating rate of 14.5 °C/min. The fraction of the resulting carbonaceous substance was 53.8 wt. %. This regime is characterized by significant gas release (12.4 wt. %). The gas includes hydrogen, carbon monoxide, hydrocarbon gases up to C_5.

A reduced heating rate (down to 12.3 °C/min) led to a decrease in gasrelease and the formation of liquid hydrocarbon products. It should be noted that tar-like mass was tapped from the bottom of the reactor at decelerated pyrolysis.

Slow pyrolysis at a heating rate of 6 °C/min within the same temperature range was accompanied by the formation of a liquid hydrocarbon mass in an amount of 2.1 wt. %. Its appearance is an oily, dark brown, homogeneous liquid with a characteristic odor of hydrocarbons. Primary tar formed at pyrolysis can give valuable products such as waxes, asphaltenes, carboxylic acids, phenols by fractional distillation.

Gas release remained at the level of fast pyrolysis. The release of liquids, including water, was slightly dependent on the regime of pyrolysis.

Analysis of the dynamics of the pyrolysis process of sludge has shown that, regardless of the heating mode, only drying of the material occurs up to 200-250 °C. The water release during this period was 60 % of the total amount of liquid. Within 600-700 °C, true pyrolysis starts to release copious products. Its intense proceeding was observed up to 780–800 °C. The yield of sludge pyrolysis products is shown in Table.

Table. Material balance of sludge pyrolysis

	Experiment 1	Experiment 2	Experiment 3	Experiment 4	Experiment 5
m(raw), g	20.6	26.1	24.4	20.8	26.3
V(gas), ml	2250	2450	2550	2550	2550
m(gas), g	2.6	2.7	2.4	2.5	2.8
V(liquid), ml	6.0	9.0	9.8	7.3	11.0
m(liquid), g	6.8	9.7	10.3	6.5	11.6
m(solid), g	11.1	13.25	11.3	10.0	11.1
w(heat), °C/min	14.5	12.3	11.4	6.6	12.3
Yield of pyrolysis products, % of raw material					
Gas	12.4	10.4	9.9	11.8	10.6
Total liquid	33.1	37.1	42.2	31.2	44.1
Solid residue	53.8	50.8	46.4	48.3	42.3
Loss	0.7	1.7	1.5	8.7	3.0

Therefore, our pyrolysis recycling of the sludge of treatment plants is waste-free.

The average composition of the products of sewage sludge pyrolysis is as follows, wt. %: char 45 %, primary tar 2.5 %, gaseous products 17.5 %, liquid products, including water, 35 %.

The gases generated during sludge pyrolysis include about 70 wt. % of combustible components and have a calorific value of 4,000 kJ/m^3. This combustible gas can serve as a fuel for the pyrolysis reactor and a heat carrier for the primary raw dryer.

The ratio of the resulting gas, tar and char mainly depended on the process temperature and the content of organic matter and moisture in the starting material.

Thus, high-temperature pyrolysis is one of the most promising methods of processing of any solid waste containing organic matter.

EFFECT OF TEMPERATURE ON ETHANOL CONVERSION OVER SURFACE OF Zr-MODIFIED ZEOLITE SYSTEM OF ZSM-5 TYPE

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Summary

A modification of high-silicon zeolite ZSM-5 by zirconium is carried out and a direction chemical conversion of ethanol on the surface of this system is studied. Shows the influence of process parameters on the direction of the transformation products of ethanol dehydration. Determine the mechanism of the formation of aromatic hydrocarbons on the surface of the system.

Introduction

One of the oldest methods of biomass treatment is the production of ethyl alcohol from it. Ethanol, in turn, can be used as motor fuel, however, due to a high hygroscopicity, such fuel can not be used at temperatures below zero. Another way is ethanol dehydration that gives the ethylene, diethyl ether or hydrocarbons of various structures. The implementation of direct conversion of ethanol and fermentation mixtures of hydrocarbons possibly on catalysts based on ZSM-5 – pentasil family of zeolites. These catalysts are used in industrial processes such as alkylation of aromatics, reforming, as well as the conversion of methanol to gasoline [1].

In zeolites type of the pentasil a key element of the crystal lattice is a fragment of the five- and six-membered rings, the combination of which gives the chain, forming layers. Within the zeolite channel system is formed, which represents a cross-section of a circular ten-membered ring diameter is 0,54-0,56 nm. The average pore size of the zeolite is such that prevents the formation of hydrocarbons having carbon atoms in the molecule is larger than 12, which provides high selectivity in the conversion of ethanol to gasoline range hydrocarbons [2-3].

Results and Discussion

With an aim of the study an catalyst activity at different temperatures in relation to the conversion of ethanol were carried out on the surface of the catalyst 1 % Zr-ZSM-5 with the silicate modulus M = 80 mol/mol, activated in flow air at a volumetric feed rate of 1 h^{-1}. The results of the chromatographic analysis of the products are shown in Table 1.

Table 1. General hydrocarbonic composition of liquid and gaseous products

Product	Weight content, %				
	300 °C	350 °C	400 °C	450 °C	500 °C
C_1-C_2	0,0	0,8	1,7	3,5	4,6
C_2H_4	1,4	0,9	0,3	0,9	1,3
C_3H_8	7,7	5,6	14,8	16,2	18,8
n-C_4-C_5	1,8	3,3	0,7	0,6	0,4
n-hexane	0,7	0,5	0,1	0,0	0,0
i-C_4-C_6	16,9	19,0	13,6	9,5	8,3
i-C_7-C_{14}	3,7	5,8	1,3	0,8	0,2
n-C_7-C_{14}	0,6	0,2	0,2	0,1	0,0
Alkenes C_4-C_6	3,6	1,5	0,1	0,2	0,2
Alkenes C_7-C_{14}	1,4	0,7	0,0	0,0	0,0
Ar-C_6-C_8	3,3	8,0	19,0	17,0	18,8
Ar-C_9-C_{14}	3,5	3,8	1,9	1,3	0,8
Naphthenes C_5-C_6	0,6	1,0	0,1	0,1	0,0
Naphthenes C_7-C_{14}	2,0	1,6	0,5	0,4	0,3
H_2O	50,5	47,2	45,6	49,2	46,1

The study of the physico-chemical characteristics of high silica zeolite and regularities of the ethanol reactions behavior allowed to propose the following scheme of conversion of hydrocarbons on the surface of the studied system.

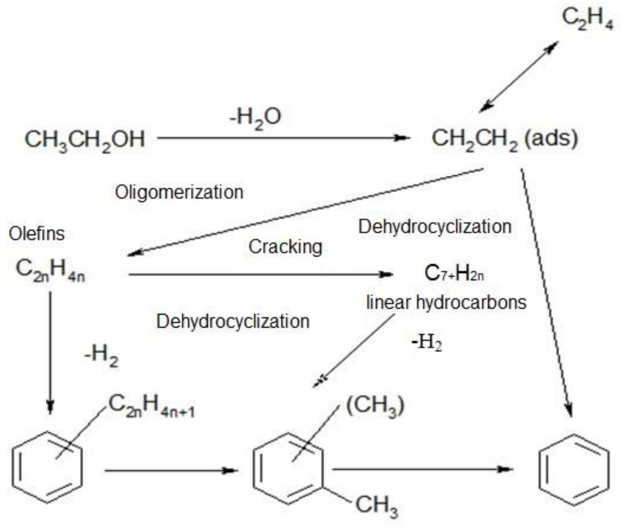

Figure 1. Scheme of ethanol conversion over catalyst

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PP-24

OXIDATIVE CONVERSION OF PROPANE-BUTANE MIXTURE TO HYDROGEN OVER POLYCOMPONENT OXIDE CATALYSTS

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Powerful raising of economy in XX century is the result of availability of oil, the main power resource of hydrocarbons and other chemicals. However the reserve of oil is not unlimited. Processing of the natural gas, containing C_3-C_4 alkanes, is actual at the present moment. The finding of ways for activation and involving in reaction of partial oxidative conversion of C_3-C_4 alkanes in view of their wide distribution in composition of natural and oil gases can be an inexhaustible source for synthesis of various products of organic synthesis. The hydrogen formed in composition of products of oxidative conversion of alkanes, represents independent interest as a marketable product. The rapt attention is given to synthesis of hydrogen and hydrogen-containing mixtures for producing of hydrogen fuels. It is necessary to note, that the hydrogen exceed on power consumption all compounds, which can serve as fuel: 2,6 times – natural gas, 3,3 times – liquid hydrocarbons of oil, 5 times – coal, 6,6 times – methanol etc. The high technologies of hydrogen power already in nearest 10 years will be a basis of development of all world economy. The hydrogen is unique ecologically clean fuel and reagent, product of which oxidation is of water vapor or liquid water [1].

The investigations were carried out on installation of a flowing type at atmospheric pressure in tubular quartz reactor with the fixed layer of the catalyst. The catalysts were characterized by XRD. The determination of surface, porosity and element content of samples are carried out. The catalysts on the basis of elements – Mo, Bi, Ce, Ni, W, Sb, Mn, Fe, Ga, and Cr were synthesized. White and red clays are used as the carriers. The temperature range was 300-600 °C at the space velocity 330-15000 h^{-1}. Reactants and products were analyzed by chromatographic method [2].

The influence of space velocity on the contents of hydrogen was investigated at oxidation of propane-butane mixture on MoCrGa/clay. 3150 h^{-1} is the optimal space velocity for hydrogen at 873 K (Table 1).

The investigation of natural clay by a XRD method have shown, that the basic phase of white clay is kaolin $Al_2(OH)_4Si_2O_5$ (ASTM-29-1488) and α-quartz SiO_2. Red clay is differed from white by the presence of hematite Fe_2O_3 and absence of α-quartz – less 1 %. The element analysis of the samples of sorbents of initial and processed by 10 % HCl has shown, that oxide compounds of Si, Al, and also Ca, Mg, Fe, Na are present mainly at samples of clay. Ratio SiO_2/Al_2O_3 (the silicon module) was 5-0,4. The silicon module grows after acid processing. The phase composition of clay after processing by a hydrochloric acid practically did not vary. Specific surface and porosity of investigated samples of sorbents were determined by low-temperature adsorption of nitrogen by BET method. It was established that the surface of clay was 10-16 m^2/g. Change of optimum radius of pores were from 2 up to 5 nm. The processing of sorbents by 10 % HCl promoted development and increase of pore radius.

Table 1. Oxidative conversion of propane-butane to hydrogen over MoCrGa/TWC catalysts. W = 3150 h^{-1}, T = 873 K, C_3-C_4; N_2:O_2:Ar = 1:1:4:, vol.

Catalyst	Yield of hydrogen, %
10 % MoCrGa/TWC	1,0
5 % MoCrGa/TWC	1,0
1 % MoCrGa/TWC	89,92

The analysis of composition of products of C_3-C_4 oxidative conversion has shown that the process carries out by complex mechanism including oxidation, oxidative dehydrogenation and cracking. Polyextreme character of change of catalytic properties in oxidation of propane-butane mixture and greatest activity of low-percentage supported catalysts are caused by existence in catalysts as crystal and amorphous phases over carriers and occurrence of strong interaction in system active phase-carrier [1,2].

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PP-25

SOLKETAL PRODUCTION BY HETEROGENEOUS CATALYSIS

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Glycerol is one of renewable resources that is produced as a waste chemical during the production of fatty acids, biofuels and biolubrificants in quantities greater than the current demand [1]. The reaction between glycerol and acetone produce solketal which can be used as solvent, surfactants, flavoring, fuel additivies, etc [2]. In Industry, solketal is producted by homogeneous catalysis using p-toluenesulfonic acid, during 12 h at 100 °C [3]. The purpose of this presentation is understand the best condition to produce solketal by heterogenous catalyst, denominated H-Beta zeolite (SAR 19), synthesized by PROCAT/UFRJ.

Experimental

A Stirred Tank Reactor (STR) with 300 milliliters of capacity, PAAR 4842 controller model, manufactured using stainless steel 316, was used to conduct the reactions. A fractional factorial design (2^{4-1}), two levels involving four variables a total of eight experiments with addition of 3 experiments at the focal points, was used as a tool to determine the best experimental conditions for the acetalization reaction of glycerol with acetone using STATISTICA Software 8. The effects of some variables which will be analyzed are responses conversion, yield and selectivity. The reactor was fed with 40 g of glycerol (0,43 mols) and the following variables were assessed: stirring (400-700 rpm), temperature (40-60 °C), the amount catalyst (1,0-5,0 % over the mass of glycerol), and the amount of acetone (in molar ratio 1:2-1:4). The reaction time was fixed in 1 hour.

Results and discussion

Looking at Table 1 results, it is simple to understand that to the conversion and yield all variables were significant and positive effects were obtained. Then in selectivity analysis only catalysis amount were significant also with positive effect, however it was expected. The best result of this fractional factorial design was entry 8. The entry 8 is characterized by the increased agitation (700 rpm) which prevents the mass transfer resistance to both internal and external; the temperature influence

Table 1: Results of experimental data design

Entry	Conversion (%)	Yield (%)	Selectivity (%)
1	23,81	22,45	94,28
2	42,23	41,46	98,16
3	63,2	61,7	97,63
4	53,12	52,1	98,09
5	59,35	57,07	96,16
6	58,98	57,91	98,19
7	60,37	58,98	97,69
8	72,61	71,39	98,31
9	57,58	56,42	97,99
10	56,52	55,26	97,77
11	54,75	53,91	98,46

directly in the reaction rate, but because it is an exothermic reaction and reversible work in milder temperatures (60 °C) to prevent the displacement direction of the reagents at the time of balance; the molar ratio of 1 : 4 will not introduce more problems, since the end of the reaction it is possible to recover the no reacted acetone and lastly the amount of catalyst to be 5 % of the initial mass of glycerol, the greater the mass glycerol more acidic sites are available for reaction when the acetalization reaction. To continue this work will target the kinetic study and the search for the activation energy value.

Conclusion

A fractional factorial design has showed the best condition of reaction system. It was found in entry 8: 72,61 % of conversion; 71,39 % of yield and 98,31 % of selectivity. The results indicated the potencial use of H-Beta zeolite (SAR 19) as a heterogeneous catalyst of acetalization reaction.

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Acknowledgements

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PP-26

STRUCTURE SENSITIVITY IN HYDROGENATION OF GALACTOSE AND ARABINOSE OVER Ru/C CATALYSTS

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Sugar alcohols can be used as alternative sweeteners, intermediates in pharmaceutical production and as humectants in cosmetics. Hydrogenation of glucose or other sugars to corresponding sugar alcohols has been actively studied over Ni and Ru catalysts. Application of Raney-type Ni catalysts has a range of disadvantages such as metal sintering and poisoning as well as nickel leaching [1-3]. As an alternative to nickel glucose hydrogenation to sorbitol over ruthenium catalysts has been actively studied [3, 4] and was shown recently [4] to be structure sensitive.

In this work, the influence of ruthenium nanoparticle size on the catalyst activity was studied in order to find an optimal Ru catalyst for hydrogenation of another sugar- galactose, which is an epimer of glucose and can be derived from hemicelluloses. In addition experiments were performed with a C5 sugar – arabinose.

A series of 3 wt. % Ru on mesoporous carbon material Sibunit catalysts were synthesized by incipient wetness impregnation using $RuCl_3 \cdot nH_2O$ as a metal precursor. To obtain samples with different Ru particle sizes the catalysts were subjected to thermal treatment under oxidizing atmosphere varying temperature and duration prior to reduction at 430 °C for 6 h. The catalysts were characterized by HRTEM and XRF. Hydrogenation of galactose and arabinose over Ru/C was carried out in a Parr 4561 autoclave at 120 °C under H_2 pressure (19 bar). Samples were periodically withdrawn and analyzed by HLPC (Biorad HPX-87C carbohydrate column) equipped with an RI detector.

As a result, Ru/C catalysts with the different particles size and distributions were synthesized and were used to explore their catalytic behavior. The results of TEM analysis are presented in Fig. 1. Note that the catalysts with the same average particle size 7.6 nm but different size distributions were obtained. Interestingly, Ru/C with monomodal and bimodal distribution showed different activity in hydrogenation of galactose, with the bimodal sample being more active than its monomodal counterpart probably due to presence of rather smaller nanoparticles in the former

(Fig. 2). The catalysts with narrow particle size distribution and similar average particle size 1.0-1.3 nm showed the same catalytic activity.

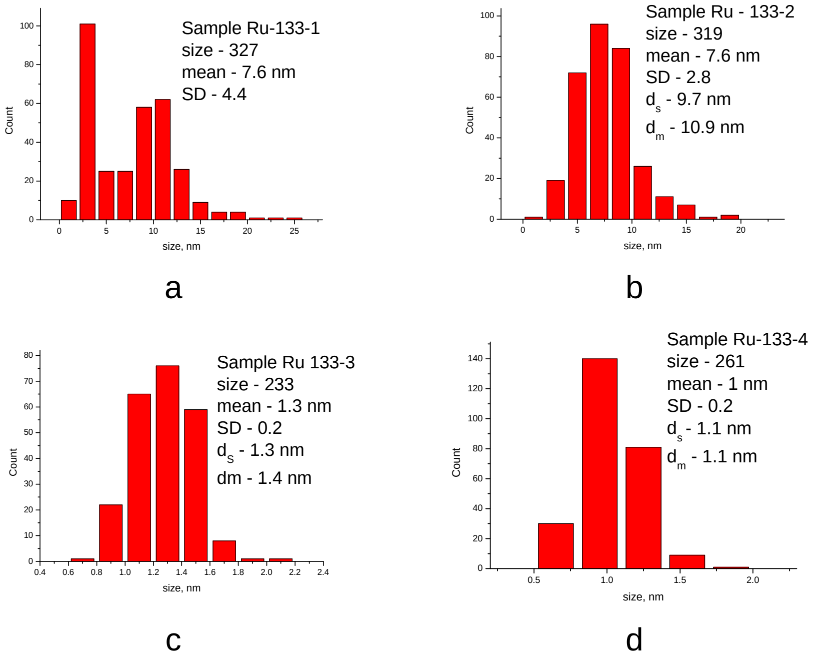

Fig. 1. TEM data for Ru/C treated in air flow at a) 300 °C for 1.5 h (*Ru-133-1*), b) 400 °C for 1.5 h (*Ru-133-2*), c) 150 °C for 1.5 h (*Ru-133-3*), d) 150 °C for 1.5 h, 200 °C for 6 h prior to the samples reduction (*Ru-133-4*)

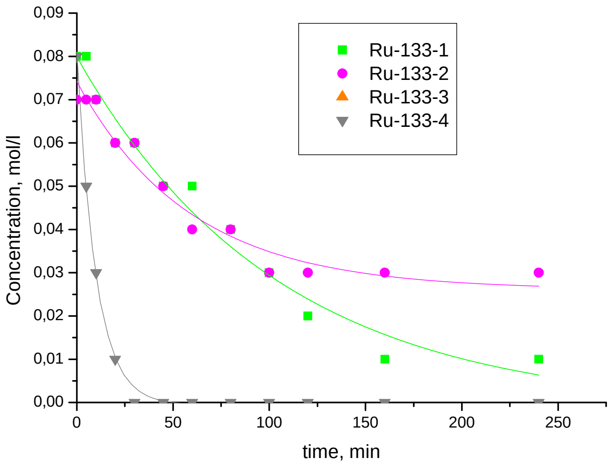

Fig. 2. Catalytic activity of Ru/C catalysts in galactose hydrogenation

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BUILDING-UP CATALYTIC APPROACHES FOR PRODUCTION OF BIOFUEL COMPONENTS FROM BIO-DERIVED OXYGENATES

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Furfural is the main industrial product of pentose carbohydrates hydrolysis, however development of biofuels of the furfural platform has started to be discussed only recently [1,2]. Blending research octane numbers (BRON) of ethyl-, propyl-, and butylfurfuryl ethers were determined as 110, 113 and 97, correspondingly, satisfieng the fuel blend composition requirements [2,3]. Recently 2-methylfuran was successfully tested in the mixtures with gasoline in car engines [4].

Hydrogen consumption is one of the main characteristics for furfural and other oxygenated products hydrogenated into biofuels. Alkylfurfuryl ethers are very attractive from this point of view (consumption of one mole of hydrogen per mole of the product). Catalytic hydrogenation of furfural dialkylacetals is considered to be a possible way to produce such ethers.

In this work, catalytic hydrogenation of furfural in different alcohol solutions was studied in order to find the influence of catalyst and alcohol types on the furfural conversion and selectivity to corresponding aimed ether.

CuRu and Pt (3-8 wt. %) catalysts supported on carbon (Sibunit, 40-70 μm fraction) were prepared by the incipient wetness impregnation followed by activation with hydrogen *in-situ* in the reactor. Hydrogenation was carried out in a batch reactor (150 ml) at 100-200 °C and hydrogen pressure of 1 MPa. 19.1 g of the alcohol (ethanol, *n*-propanol or *n*-butanol), 0.53 g of furfural, and 0.2-0.4 g of the catalyst were charged in the reactor and heated during 6 hours. The products were analyzed by GLC and GC-MS (VG-7070 GC/MS and Agilent 5973N EI/PCI).

Accoding to GLC analysis data catalytic hydrogenation of furfural in alcohol media is accompanied by the equilibrium limited acetal formation, when furfural conversion into the corresponding acetals achieves 55-66 %. In the case of *n*-propanol and *n*-butanol media this equilibrium leads to further hydrogenation of dipropyl- and dibutylacetals into the corresponding furfuryl ethers with yield 19 %. It should be noted, that at low furfural conversions (~ 20 %) in the presence of CuRu/C catalyst selectivity to butylfurfuryl is more than 50 %. A similar possibility of *t*-5-butoxymethylfurfuryl dibutyl acetal hydrogenation into the corresponding ether 2,5-dibutoxymethylfuran, was recently demonstrated [5,6].

The yield of furfuryl alcohol does not exceed 8-30 %. It was shown that furfuryl alcohol could not alkylate propanol under these conditions, and the yield of propylfurfuryl ether did not exceed 5 %. This indicates that furfuryl alcohol is a side product but not an intermediate generated alkylfurfuryl ethers upon alkylation with propanol or butanol. Probably, the difficulties of direct alkylation of furfuryl alcohol result from its conversion into levulinic acid and tar.

Therefore it was shown that furfural hydrogenation in alcohol media is accompanied by formation of acetals. Both products, furfural and furfuryl acetals, could be hydrogenated giving the corresponding ethers in the latter case. The furfuryl ethers produced over CuRu and Pt catalysts, namely butylfurfuryl ether, propylfurfuryl ether, 2-methylfuran, and furfuryl alcohol are characterized with high anti-knocking activity (BRON above 100) and could be applied as alternative components of biofuels.

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PP-28

DEHYDRATION OF METHYL LACTATE TO ACRYLIC ACID USING CALCIUM-PHOSPHATE-SILICA CATALYSTS

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Development of the production of multifunctional organic acids in low-cost, high-efficiency processes of carbohydrates fermentation makes available a new route to chemical production from biomass. Lactic acid is approaching large-scale production via fermentation and show particularly excellent promise as feedstocks for catalytic conversion routes such as hydrogenation, dehydration, or condensation (Figure 1).

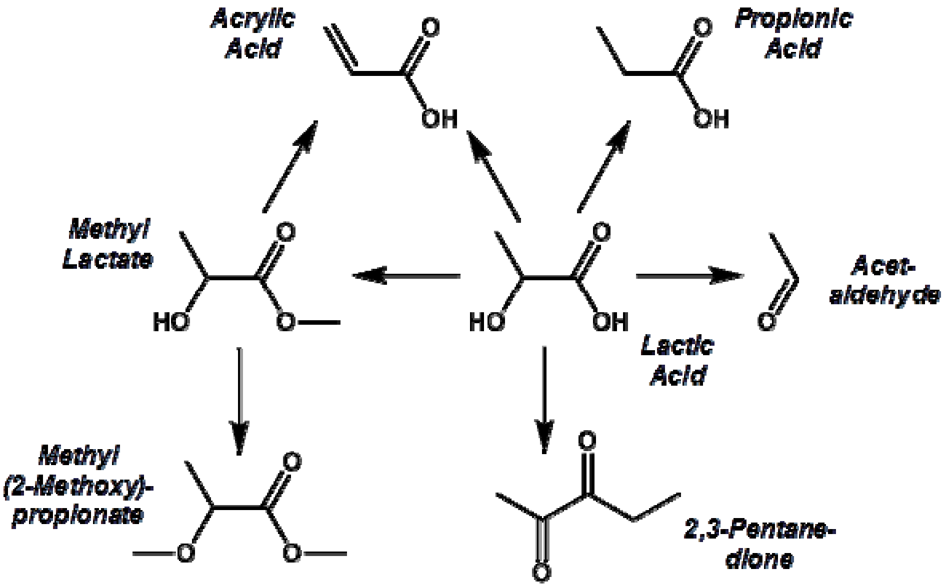

Fig. 1. Possible scheme for chemicals based on lactate feedctocks

In particular, it looks attractive at least partial redirecting of producing conventional petrochemicals such as acrylate monomers to renewable feedstocks. A bottle neck for implementing this technology is the development of effective catalysts of lactate materials dehydration. This study investigated methyl lactate dehydration over various calcium-phosphate-silica catalysts under various conditions [1].

Catalysts $Ca_3(PO_4)_2/SiO_2$, $CaHPO_4/SiO_2$, $Ca(H_2PO_4)_2/SiO_2$ и $Ca_2P_2O_7/SiO_2$ with different ratio of corresponding calcium phosphate component vs silica (from 90/10 to 60/40 wt. %) was prepared by precipitation method followed by water rinsing to remove soluble impuritgies. Samples obtained was dried at 120 °C and then calcined at 480 °C in air. Catalysts obtained were characterized by XRD and FTIR methods and the specific surface areas and pore volumes of catalysts were measured.

The dehydration of methyl lactate over the catalysts was carried out in a fixed-bed quartz reactor operated at 350-420 °C and atmospheric pressure. The feedstock (20–50 wt. % aqueous solutions of methyl lactate) was pumped into the preheating zone of reactor and driven through the catalyst bed by nitrogen. Regulating the nitrogen flow rate it was maintained hold-up time 0.5-1 s. Analysis of the products was carried out by GC and GC-MS methods.

The data of experiments on dehydration of methyl lactate showed that, regardless of the structure of calcium phosphate component, the highest efficiency is typical for samples with ratio ‘$Ca–PO_x/SiO_2$’ = 80/20 wt. %. The methyl lactate conversion over the catalyst $Ca_2P_2O_7/SiO_2$ (80/20 wt. %) at 390 °C, methyl lactate content in feedstock 20 wt. % and hold-up time 1 s was 75 % and acrylates selectivity was 49 %.

Side reactions of condensation and polymerization lead to coke deposition, resulting in catalyst deactivation. Complete catalyst regeneration and activity recovery is achieved by calcination it in air at 480 °C.

From XRD and FTIR data was found that freshly prepared catalysts based on calcium hydrophosphates decomposed during calcination to form ultimately pyrophosphate structure. During the regeneration of these catalysts as well as $Ca_2P_2O_7/SiO_2$ pyrophosphate structure is preserved.

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PP-29

THE ROLE OF MODIFIERS IN MULTI-COMPONENT Au/Al_2O_3 CATALYSTS DESIGNED FOR PREFERENTIAL CO OXIDATION

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Introduction

Al_2O_3 supported gold catalysts modified by Pb, Cu, Ce and Sm, have been investigated in order to elucidate the beneficial role of modifiers in preferential CO oxidation. The multi-component catalysts have been compared to catalysts containing no or less number of modifiers.

Experimental

All catalysts have been prepared by homogeneous precipitation of nitrate precursors using urea as precipitating agent. Catalytic properties and characteristic features of catalysts were investigated in a 16-channel SS continuous-flow gas phase reactor connected to a quadrupole mass spectrometer. Different spectroscopic techniques (XPS, FTIR), XRD and HRTEM measurements were applied for catalyst characterization.

Results

From the catalytic results emerges that upon the addition of modifiers both CO conversion and the selectivity of oxygen towards CO oxidation increases. A high catalytic activity can be observed on Au-Pb two component catalysts, where the formation of alloy between Au and Pb can be concluded. The best catalyst compositions obtained consisted of AuPbCu. Further slight improvement in catalytic performance, especially in selectivity, has been achieved by addition of Sm and Ce to the three component AuPbCu catalyst (Table 1).

Table 1. The conversion (α_{CO}) and selectivity (S_{CO}) obtained over prepared catalysts

Sample	α_{CO}	S_{CO}
Au	84	44
AuPb	100	53
AuPbCu	97	64
AuPbCuCe	94	79
AuPbCuCeSm	93	76

According to FTIR spectroscopy of CO adsorption over the different catalysts, in the presence of Cu modifier the intensity of carbonyl band increased substantially. For the catalysts with more than 3 components the intensity of CO adsorption in the presence of O_2 and H_2 increases about 3 or 4 times compared to the CO adsorption in their absence. In the presence of Pb modifier a band appeared at 2033 cm^{-1} wavenumbers that can be assigned to a catalytically highly active CO adsorbed on Au-Pb alloy (Figure 1). In the presence of O_2 this band disappeared because the activated CO reacts with the O_2.

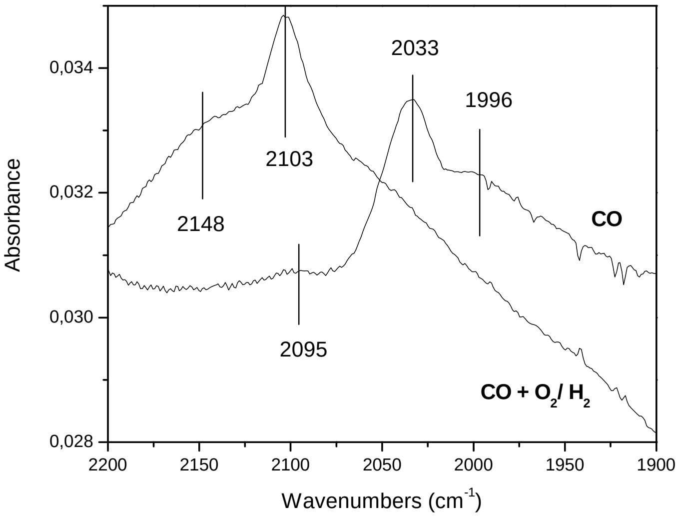

Figure 1. FTIR spectra of CO adsorption over Au-Pb/Al_2O_3 catalyst

The XPS measurements revealed that the reduction of sample resulted in Au-Pb formation, which surface is transformed to PbO_2 during the PROX reaction. The hydrogen adsorption over Au-Pb alloy is suppressed in comparison to monometallic Au, that resulted the higher selectivity.

Based on XRD ahd HRTEM measurements alloy formation can be observed in the Au-Pb and Au-Cu samples that resulted an atomic contact between the active components.

The different metal oxide modifiers provide favourable adsorption sites for oxygen thus enhancing the surface oxygen concentration. Due to the atomic contact between the oxide modifiers and gold the formation of metal ion – gold nanocluster ensemble sites has a strong contribution to the activation of CO over the multi-component catalyst[1,2].

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AQUEOUS PHASE REFORMING OF BIOMASS COMPOUNDS OVER Pt AND Ru CONTAINING CATALYSTS

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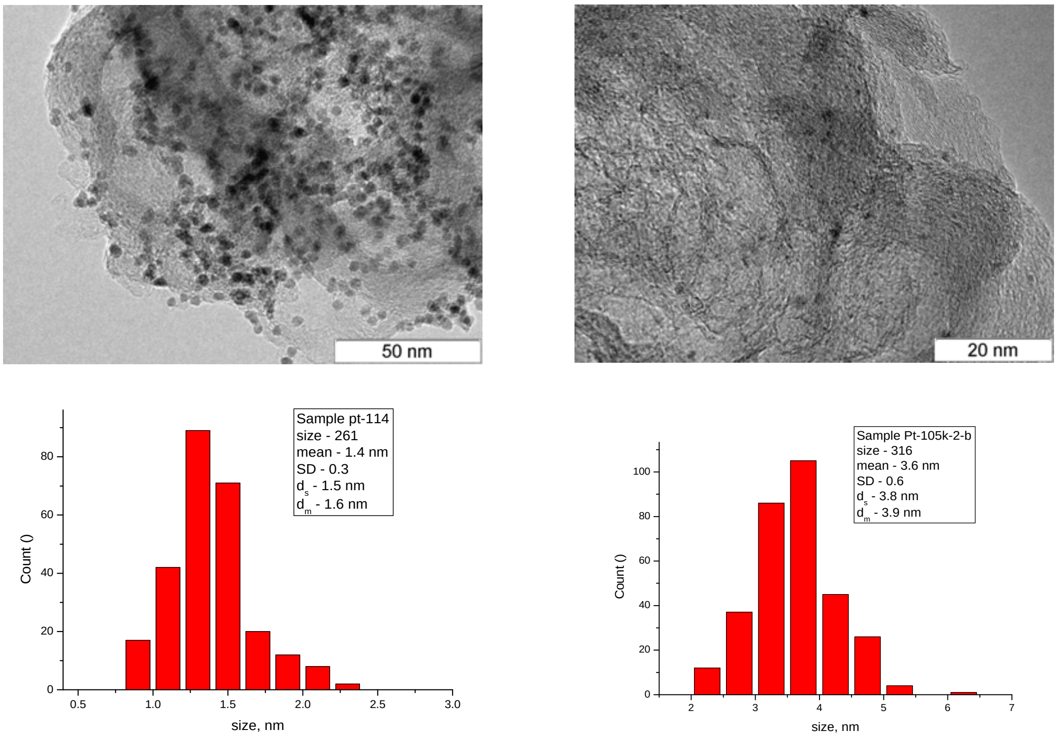
Biomass can be regarded as a renewable source of platform chemicals, biofuels and energy-rich materials [1-4]. Aqueous phase reforming (APR) has attracted a lot of attention, since this process is efficient and tunable in terms of hydrogen and light hydrocarbons production from biomass-derived compounds. The catalysts based on VIII group metals were shown to be effective for APR with Pt being the most active for APR of polyols among the monometallic catalysts [5]. At the same time, Ru was shown recently to be a more suitable catalyst due to its higher activity for C-C cleavage in the case of light oxygenates such as acetic acid [6].

In the current work catalytic behavior of Ru and Pt as well as mixed RuPt carbon-supported catalysts was studied with the general aim to relate activity/selectivity with the catalyst parameters. Besides incipient wetness impregnation (IWI), also a colloidal method, which is an effective approach to synthesis of supported metal catalysts with controllable particle size, was applied for catalyst preparation. For the colloidal method the effect of reduction temperature, the ratio between the active metal and the stabilizing agent (PVP) as well as scaling-up issues were investigated to explore regularities of metal nanoparticles (NPs) formation and to develop an approach to the synthesis of stable metal NPs with a controllable particle size. The catalysts were characterized by HRTEM, XPS, TPR, XRF, UV-Vis spectroscopy, and XRD. The APR of C2-C3 oxygenates was carried out in a continuous flow reformer equipped with total organic carbon analyzer (TOC) and gas chromatograph (Micro-GC, MS5 and PPQ columns). Composition of the liquid phase was analyzed by high pressure liquid chromatograph (HPLC, RID-10A detector and Aminex HPX-87H (300x7.8 mm) column). Typically the reaction was performed at 225-250 °C under 35-60 bar of overall pressure.

According to HRTEM analysis all prepared Pt and Ru catalysts contained metal clusters of the size 1-4 nm with a narrow NPs size distribution (Figure 1).



a b

Figure 1: TEM images and histogram of particles size distribution of Pt catalysts synthesized by IWI (a) and colloidal method (b)

The catalytic activity of Ru and Pt deposited on mesoporous carbon Sibunit by different methods was explored in APR of light oxygenates, including acetic acid, hydroxyacetone, and ethylene glycol. Comparable activity was observed over Pt/C and PtRu/C synthesized by IWI in APR of hydroxyacetone, whereas the highest selectivity to hydrogen was achieved with Pt/C catalyst.

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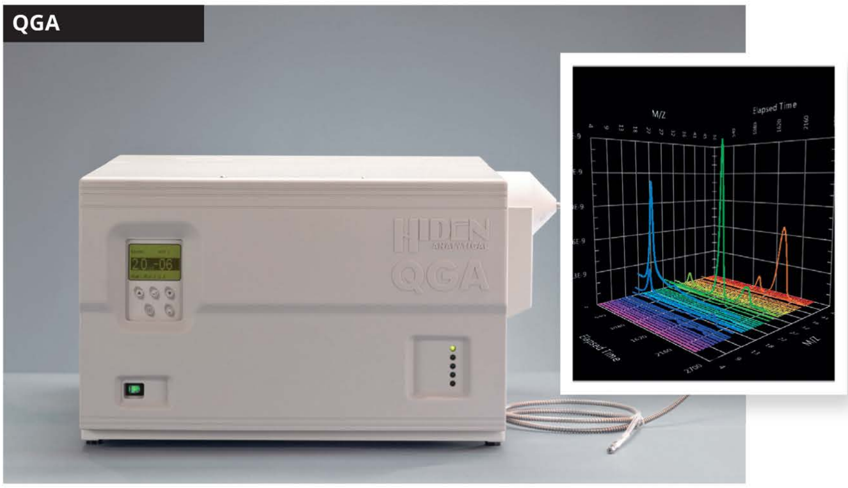
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CONTENT

ORAL PRESENTATIONS

ORAL PRESENTATIONS

ORAL PRESENTATIONS

ORAL PRESENTATIONS

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